Modeling Chemical Reactions with CFD

Reacting Flows - Lecture 10

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Outline

- Source terms in the species transport equation.
- Chemical kinetics and reaction rates.
- Subgrid scale effects.
- Reaction models and the effects of turbulence.
- Examples:
  - Stirred tank.
  - Catalytic converter.
  - Polymerization reactor.

Species transport and reaction

- The i^{th} species mass fraction transport equation is:

$$\frac{\partial}{\partial t}(\rho Y_i) + \frac{\partial}{\partial x_j}(\rho\ u_j Y_i) = \frac{\partial}{\partial x_j}\left(\rho D_i \frac{\partial Y_i}{\partial x_j}\right) + R_i + S_i$$

Rate of change + **Net rate of flow (convection)** = **Rate of change due to diffusion** + **Rate of change due to reaction sources** + **Rate of change due to other sources**

- The mass fraction of chemical species i is Y_i.
- The velocity is u_j.
- D_i is the diffusion coefficient.
- R_i is the reaction source term. *Chemical reactions are modeled as source terms in the species transport equation.*
- S_i includes all other sources.

Source of species

- The net source of chemical species i due to reaction R_i is computed as the sum of the reaction sources over the N_R reactions that the species participate in:

$$R_i = M_{w,i} \sum_{r=1}^{N_R} \hat{R}_{i,r}$$

$M_{w,i}$ *is the molecular weight of species i*

$\hat{R}_{i,r}$ *is the molar rate of creation / destruction of species i in reaction r*

- Reaction may occur as a volumetric reaction or be a surface reaction.

- Note: source terms are also added to the energy equation to take heat of reaction effects into account.

Chemical kinetics

- The r^{th} reaction can be written as: $\sum_{i=1}^{N} \nu'_{i,r} \mathcal{M}_i \underset{k_{b,r}}{\overset{k_{f,r}}{\rightleftharpoons}} \sum_{i=1}^{N} \nu''_{i,r} \mathcal{M}_i$

$$
\begin{array}{lcl}
\mathcal{M}_i & = & \text{symbol denoting species } i \\
N & = & \text{number of chemical species in the system} \\
\nu'_{i,r} & = & \text{stoichiometric coefficient for reactant } i \text{ in reaction } r \\
\nu''_{i,r} & = & \text{stoichiometric coefficient for product } i \text{ in reaction } r
\end{array}
$$

- Example: $\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}$

$$
\begin{array}{llll}
M_1 = CH_4 & M_2 = O_2 & M_3 = CO_2 & M_4 = H_2O \\
\nu'_{1,r} = 1 & \nu'_{2,r} = 2 & \nu'_{3,r} = 0 & \nu'_{4,r} = 0 \\
\nu''_{1,r} = 0 & \nu''_{2,r} = 0 & \nu''_{3}, r = 1 & \nu''_{4,r} = 2
\end{array}
$$

Reaction rate

- The molar reaction rate of creation/destruction of species *i* in reaction *r* is given by:

$$\hat{R}_{i,r} = \Gamma \left(\nu''_{i,r} - \nu'_{i,r} \right) \left(k_{f,r} \prod_{j=1}^{N_r} \left[C_{j,r} \right]^{\eta'_{j,r}} - k_{b,r} \prod_{j=1}^{N_r} \left[C_{j,r} \right]^{\eta''_{j,r}} \right)$$

$$\begin{aligned}
N_r &= \text{number of chemical species in reaction } r \\
C_{j,r} &= \text{molar concentration of each reactant and product} \\
&\quad\ \text{species } j \text{ in reaction } r \ (\text{kgmol/m}^3) \\
\eta'_{j,r} &= \text{forward rate exponent for each reactant and product} \\
&\quad\ \text{species } j \text{ in reaction } r \\
\eta''_{j,r} &= \text{backward rate exponent for each reactant and product} \\
&\quad\ \text{species } j \text{ in reaction } r
\end{aligned}$$

- Γ represents the effect of third bodies (e.g. catalysts) on the reaction rate:

$$\Gamma = \sum_{j}^{N_r} \gamma_{j,r} C_j$$

Here, $\gamma_{j,r}$ is the third-body efficiency of the j^{th} species in the r^{th} reaction.

Reaction rate constant

- The forward rate constant for reaction r, $k_{f,r}$ is computed using an expanded version of the Arrhenius expression:

$$k_{f,r} = A_r T^{\beta_r} e^{-\frac{E_r}{RT}}$$

A_r = pre-exponential factor

E_r = activation energy

R = universal gas constant = 8313 J/kgmol K

T = temperature

β_r = temperature exponent

- If applicable, the backward rate constant for reaction r, $k_{b,r}$ is computed from the forward rate constant using the relationship: $k_{b,r} = k_{f,r} / K_r$.
- K_r is the equilibrium constant for reaction r, which follows from the thermodynamic properties of the materials.

Reaction rate: the Arrhenius equation

- The Arrhenius equation is a formula for the temperature dependence of a chemical reaction rate. Originally it did not include the term T^{β}, which was added later by other researchers.

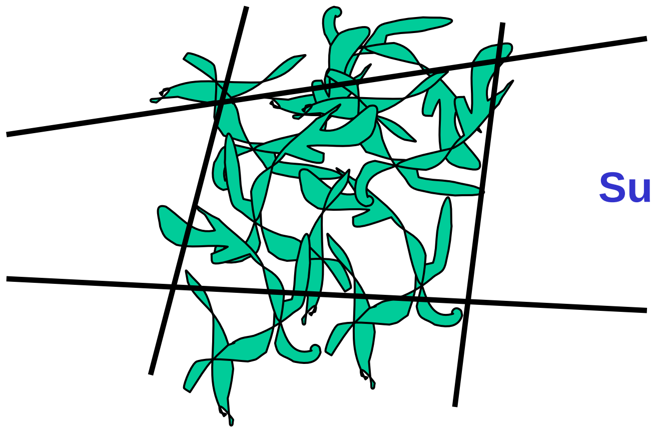
$$R_k \quad \propto \quad e^{-\frac{E}{RT}}$$

- R_k is the Arrhenius reaction rate, E is the activation energy, R is the universal gas constant, and T is the temperature.
- First proposed by the Dutch chemist J. H. van 't Hoff in 1884.
  - Won the 1901 Nobel prize in chemistry for his discovery of the laws of chemical dynamics and osmotic pressure in solutions.

- Five years later (1889), the Swedish chemist Svante Arrhenius provided a physical justification and interpretation for it.
  - Also won the 1903 Nobel prize in chemistry for his electrolytic theory of dissociation and conductivity.
  - He had proposed that theory in his 1884 doctoral dissertation. It had not impressed his advisors who gave him the very lowest passing grade.

Subgrid effects

- For each grid cell the molecular reaction rate can be calculated using the equations presented.
- What if there are concentration variations smaller than the size of the grid cell?



Subgrid scale variations

- Reaction rates calculated at the average concentrations may be overpredicted.
- For turbulent flows, models exist that take turbulent mixing effects at subgrid scales into account.

Effect of temperature fluctuations

- Temperature may vary in time, and also in space at scales smaller than a grid cell.
- What happens if we model a system as steady state and use average temperatures to predict the reaction rates?
- Reaction rate terms are highly nonlinear:

$$R_k \propto T^{\beta_k} e^{-E_k/RT}$$

$$\Rightarrow$$

$$\bar{R}_k \neq R_k(\bar{T})$$

- Cannot neglect the effects of temperature fluctuations on chemical reaction rates.

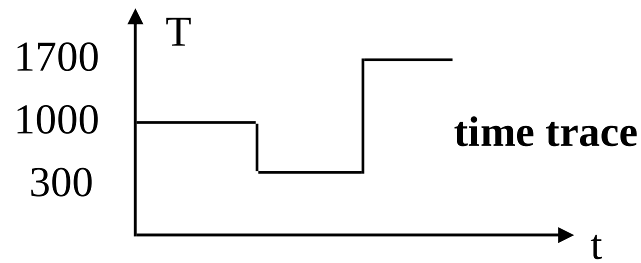
Effect of temperature fluctuations - example

- Single step methane reaction (A=2E11, E=2E8):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$R_{CH_4} = \tfrac{1}{2} R_{O_2} = -R_{CO_2} = -\tfrac{1}{2} R_{H_2O} = -A\exp(-E/RT)\,[CH_4]^{0.2}[O_2]^{0.3}$$

- Assume turbulent fluid at a point has constant species concentration at all times, but spends one third its time at T=300K, T=1000K and T=1700K.



- Calculate the reaction rates:

T(K)	300	1000	1700
A exp(-E/RT)	2.97E-24	7.12	1.43E+05

$$\overline{R}_k = 4.8E4 \neq R_k(\overline{T}) = 7.12$$

- Conclusion: just using the average temperature to calculate reaction rates will give wrong results $\rightarrow$ special reaction models needed.

Laminar finite-rate model

- Reaction rates are calculated using the molecular reaction kinetics.
  - Using average species concentration in cell.
  - Using average temperature in cell.
  - No corrections are made for subgrid scale temperature or species concentration variations.
- The mesh and, for transient flows, the timestep should be small enough to properly resolve all spatial and temporal variations.
- This may lead to very fine mesh and timestep requirements.
- If the numerical model is too coarse, species mixing and reaction rates will be overpredicted.

Viscous flow with fine striations

Effects of turbulence

- In turbulent flows, subgrid and temporal variations in temperature and species concentration are related to the structure of turbulence.
- We already solve for the effect of turbulence on the mean flow using turbulence models.
- This information can then also be used to predict the effects of turbulence on the reaction rate.
  - Usually subgrid scale non-uniformities in the species concentration (i.e. poor mixing) result in an effective reaction rate that is lower than the molecular rate kinetics based on average concentrations.
- Different reaction models exist for different systems.

Reaction models in FLUENT

- Surface reactions:
  - Particle surface reactions (e.g. coal combustion).
  - Surface reactions at solid (wall) boundaries (e.g. chemical vapor deposition).
- Combustion or infinitely fast chemistry:
  - Pre-mixed combustion models.
  - Non pre-mixed combustion models.
  - Partially pre-mixed combustion models.
  - Finite-rate kinetics in turbulent flames (composition PDF transport model).
- Finite-rate chemistry based on extended Arrhenius equation:
  - Laminar finite-rate model.
  - Finite-rate/eddy-dissipation.
  - Eddy-dissipation.
  - Eddy-dissipation concept (EDC).

The eddy-dissipation model

- A model for the mean reaction rate of species i, R_i based on the turbulent mixing rate.
- Assumes that chemical reactions occur much faster than turbulence can mix reactants and heat into the reaction region (Da >> 1).
- A good assumption for many combustors: most useful fuels are fast burning.
- For fast reactions the reaction rate is limited by the turbulent mixing rate.
- The turbulent mixing rate is assumed to be related to the timescale of turbulent eddies that are present in the flow.
- Concept originally introduced by Spalding (1971) and later generalized by Magnussen and Hjertager (1976).
- The timescale used for this purpose is the so-called eddy lifetime, $\tau = k/\varepsilon$, with k being the turbulent kinetic energy and ε the turbulent dissipation rate.
- Chemistry typically described by relatively simple single or two step mechanism.

The eddy-dissipation model

- The net rate of production of species i due to reaction r, $R_{i,r}$ is given by the smaller (i.e. limiting value) of the two expressions below.
- Based on mass fraction of reactants: $R_{i,r} = \nu'_{i,r} M_{w,i} A \rho \frac{\epsilon}{k} \min_{\mathcal{R}} \left(\frac{Y_{\mathcal{R}}}{\nu'_{\mathcal{R},r} M_{w,\mathcal{R}}} \right)$
- Based on mass fraction of products: $R_{i,r} = \nu'_{i,r} M_{w,i} A B \rho \frac{\epsilon}{k} \frac{\sum_P Y_P}{\sum_j^N \nu''_{j,r} M_{w,j}}$
- Here:

k	-	turbulence kinetic energy
ε	-	turbulence dissipation rate
Y_P, Y_R	-	mass fraction of species
A	-	Magnussen constant for reactants (default 4.0)
B	-	Magnussen constant for products (default 0.5)
$M_{w,i}$	-	molecular weight
(R), (P)	-	reactants, products

- Note that kinetic rates are not calculated!

Finite-rate/eddy-dissipation model

- The eddy-dissipation model assumes that reactions are fast and that the system is purely mixing limited.
- When that is not the case, it can be combined with finite-rate chemistry.
- In FLUENT this is called the finite-rate/eddy-dissipation model.
- In that case, the kinetic rate is calculated in addition to the reaction rate predicted by the eddy-dissipation model.
- The slowest reaction rate is then used:
  - If turbulence is low, mixing is slow and this will limit the reaction rate.
  - If turbulence is high, but the kinetic rate is low, this will limit the reaction rate.
- This model can be used for a variety of systems, but with the following caveats:
  - The model constants A and B need to be empirically adjusted for each reaction in each system. The default values of 4 and 0.5 respectively were determined for one and two-step combustion processes.
  - The model always requires some product to be present for reactions to proceed. If this is not desirable, initial mass fractions of product of 1E-10 can be patched and a model constant B=1E10 used.

Example: parallel competitive reactions

- Stirred tank system with parallel-competitive reactions:

$$\mathbf{A} + \mathbf{B} \xrightarrow{k_1} \mathbf{R}$$

$$\mathbf{B} + \mathbf{R} \xrightarrow{k_2} \mathbf{S}$$

- Reaction 1 is fast (k_1=7300 m^3/Mole.s) and reaction 2 is slow (k_2=3.5 m^3/Mole.s).
- The side-product **S** is only formed in regions with excess **B** and depleted from **A**, i.e. poorly mixed regions.
- The final product is characteried by the product distribution X:

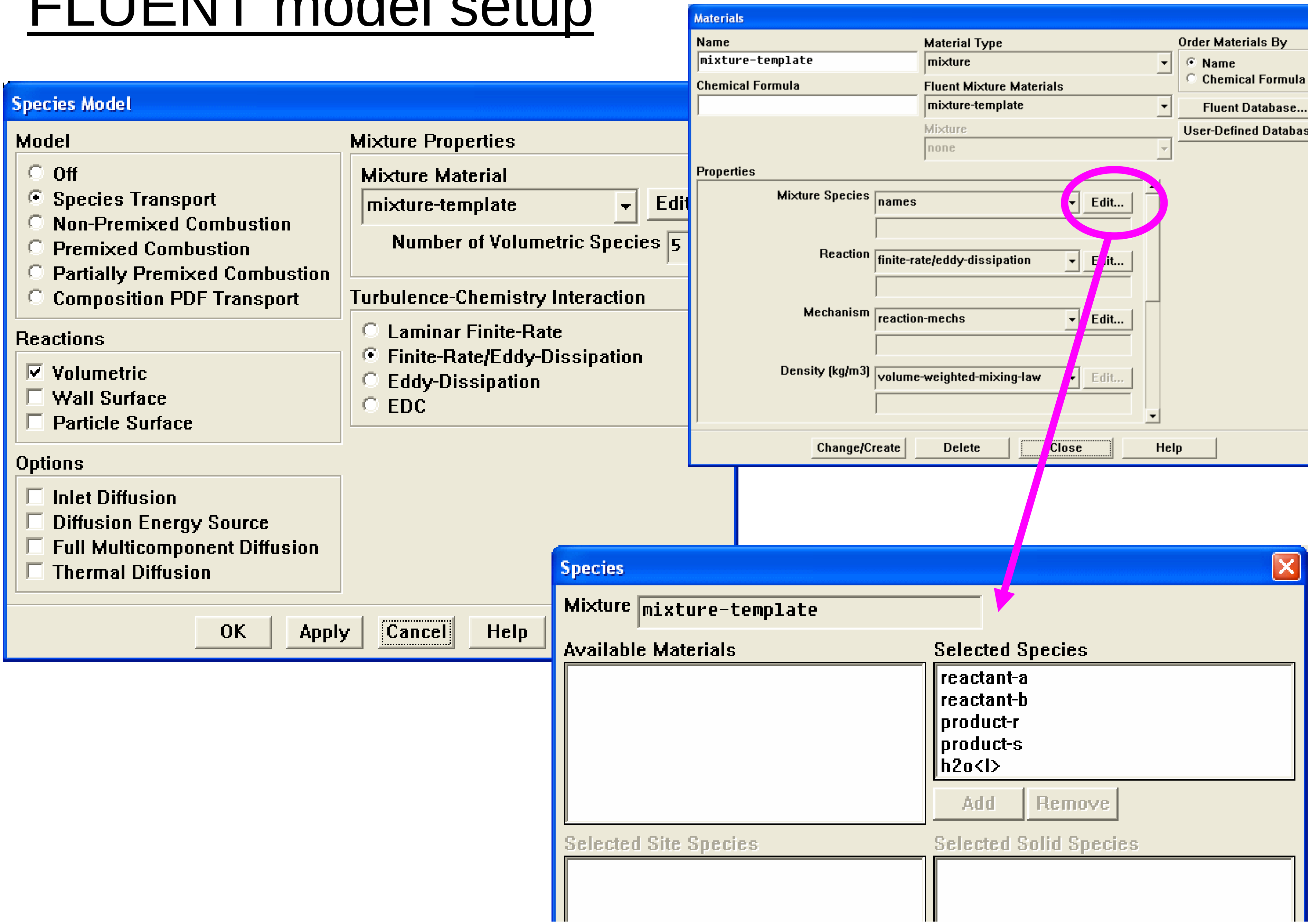
$$X = \frac{2C_S}{C_R + 2C_S}$$

- This indicates which fraction of reactant **B** was used to create side-product. A lower X indicates less **B** was used to create side-product.

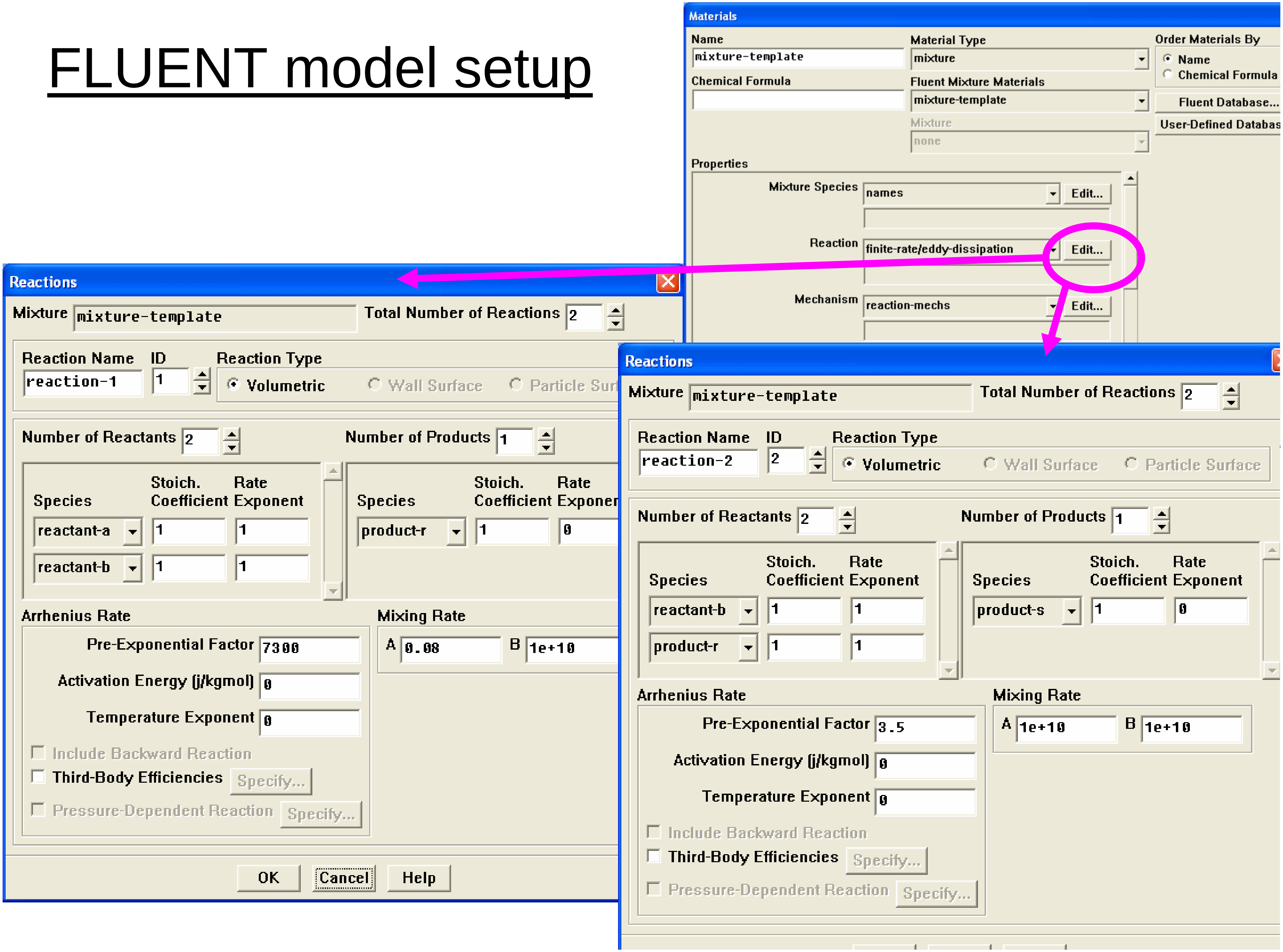
Using the finite-rate/eddy-dissipation model

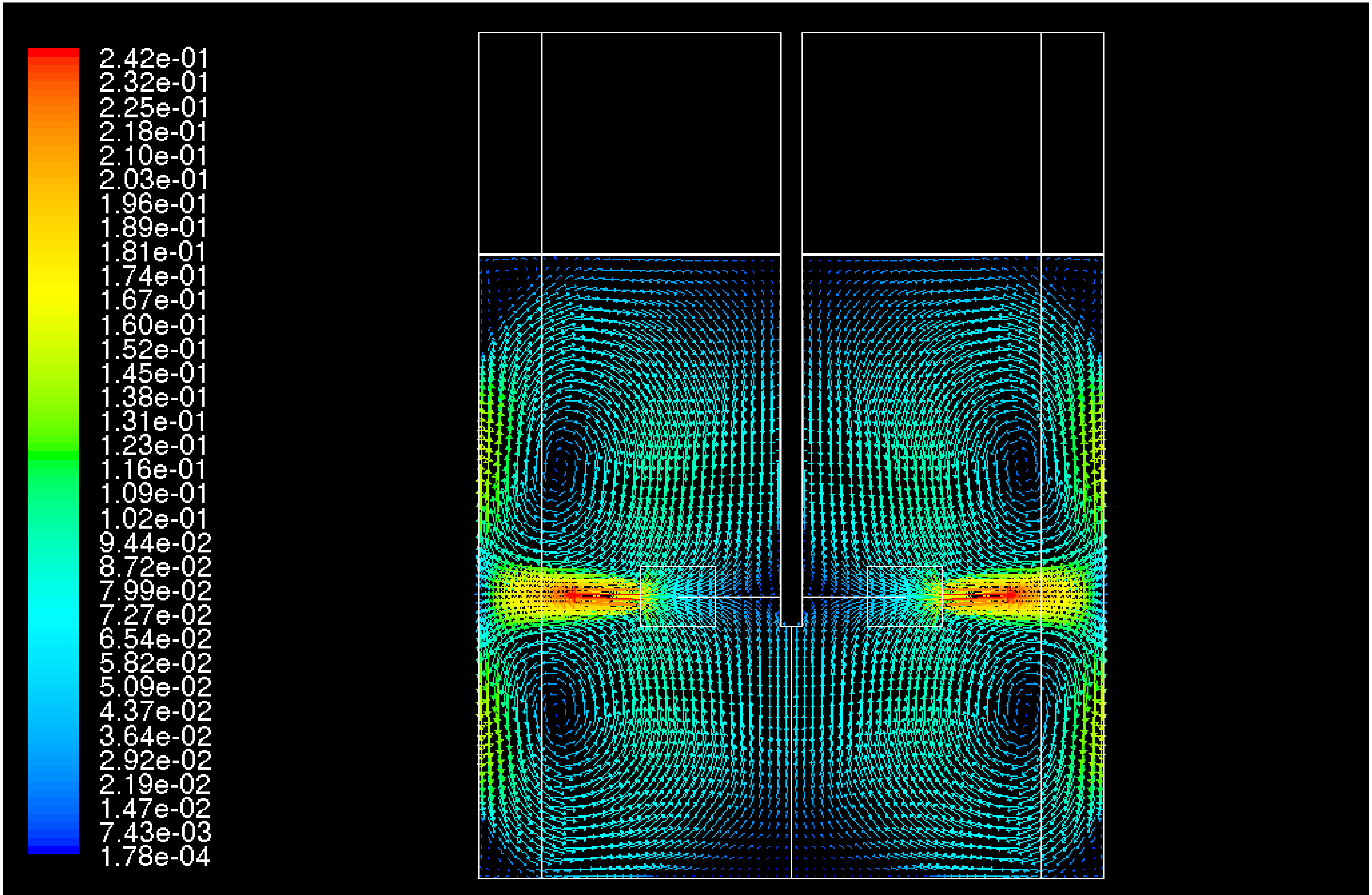
- This system was previously investigated.
- The following Magnussen model constants were determined to give good results for this system:
  - Reaction 1: model constant A_1=0.08.
  - Reaction 2: model constant A_2=1E10.
  - For both reactions, use model constant B=1E10 and initial product mass fractions of 1E-10 to disable the product mass fraction based reaction rate limiter.
  - The net effect of this set of model constants is that only the first reaction is limited by mixing rate, but not the second reaction.
- The reaction rates were set independent of temperature by specifying zero values for the activation energy and the temperature exponent.

FLUENT model setup

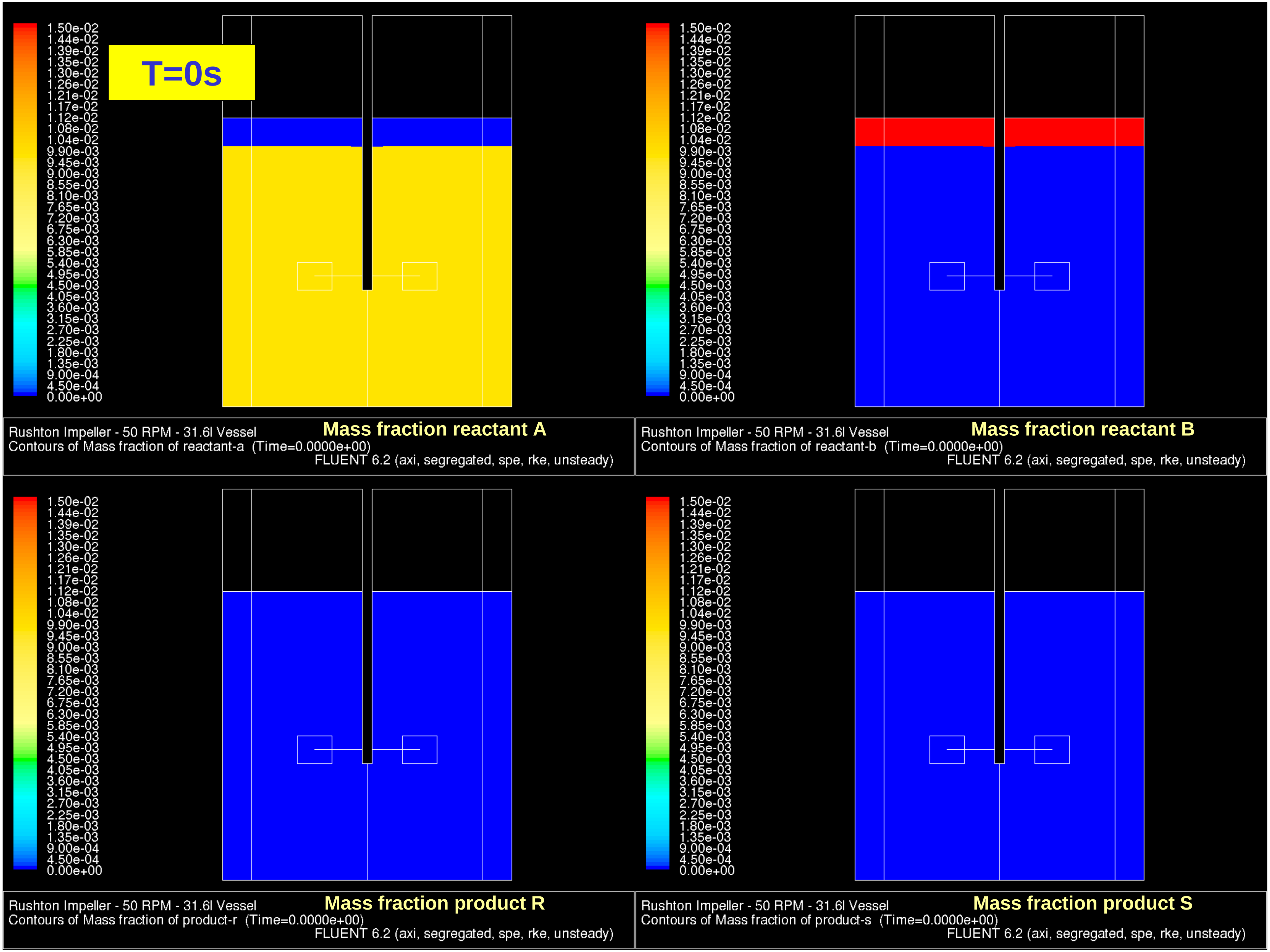


FLUENT model setup





Rushton Impeller - 50 RPM - 31.6l Vessel
Velocity Vectors Colored By Velocity Magnitude (m/s)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1.08e-02
1.04e-02
9.90e-03
9.45e-03
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8.55e-03
8.10e-03
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6.30e-03
5.85e-03
5.40e-03
4.95e-03
4.50e-03
4.05e-03
3.60e-03
3.15e-03
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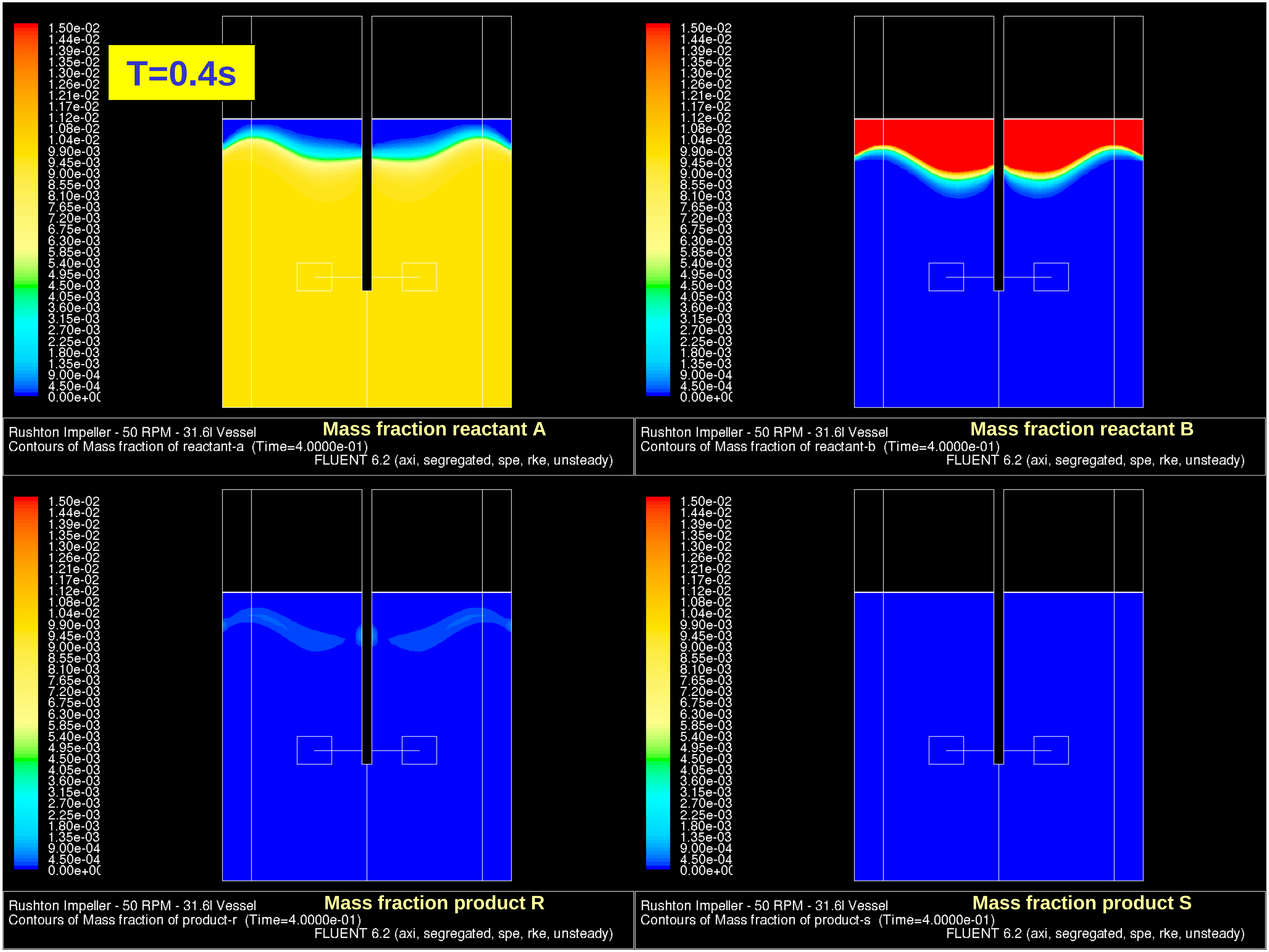
2.25e-03
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant A
Contours of Mass fraction of reactant-a (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant B
Contours of Mass fraction of reactant-b (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product R
Contours of Mass fraction of product-r (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product S
Contours of Mass fraction of product-s (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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1.04e-02
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9.00e-04
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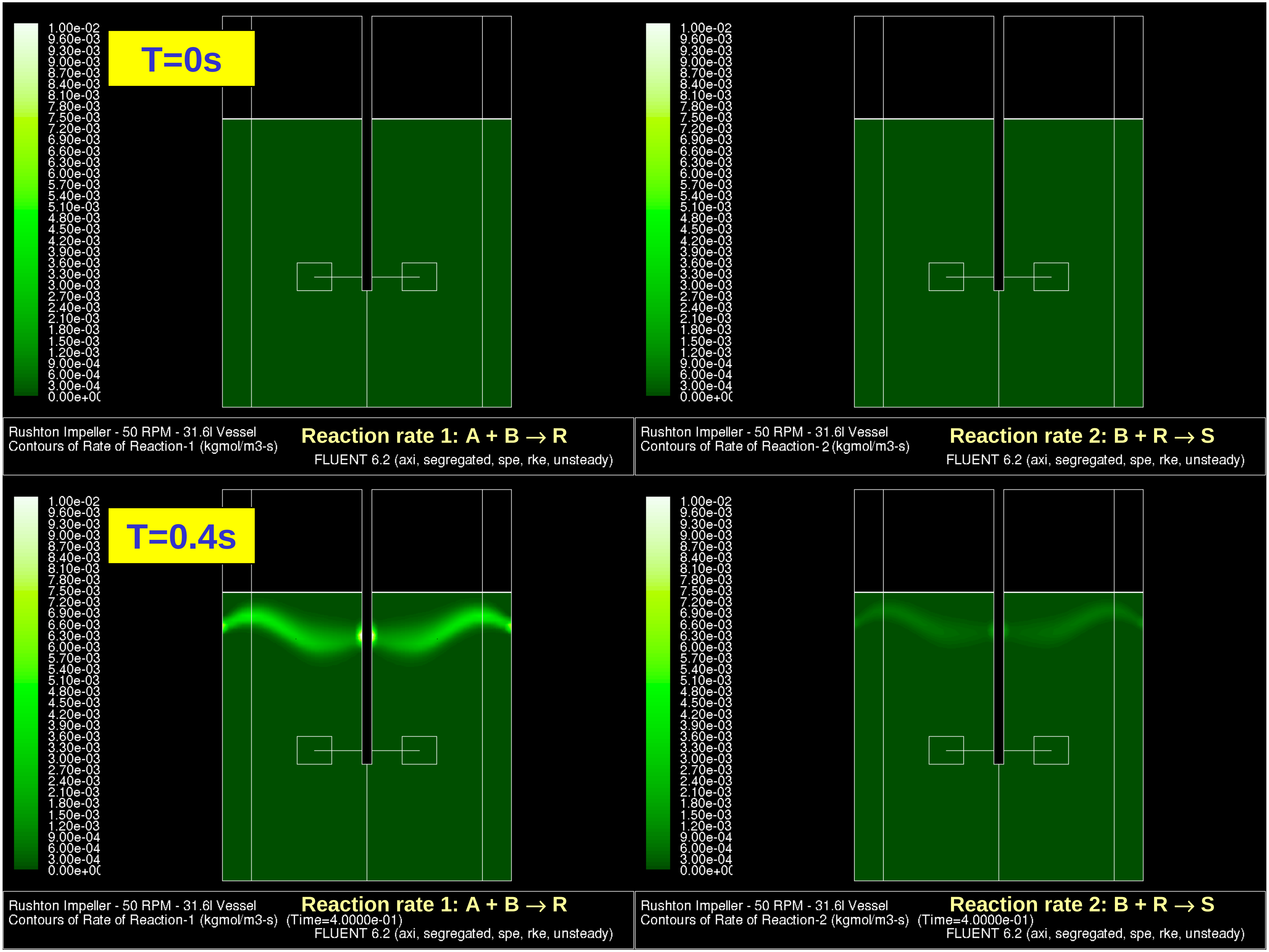
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant A
Contours of Mass fraction of reactant-a (Time=4.0000e-01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant B
Contours of Mass fraction of reactant-b (Time=4.0000e-01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product R
Contours of Mass fraction of product-r (Time=4.0000e-01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product S
Contours of Mass fraction of product-s (Time=4.0000e-01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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2.10e-03
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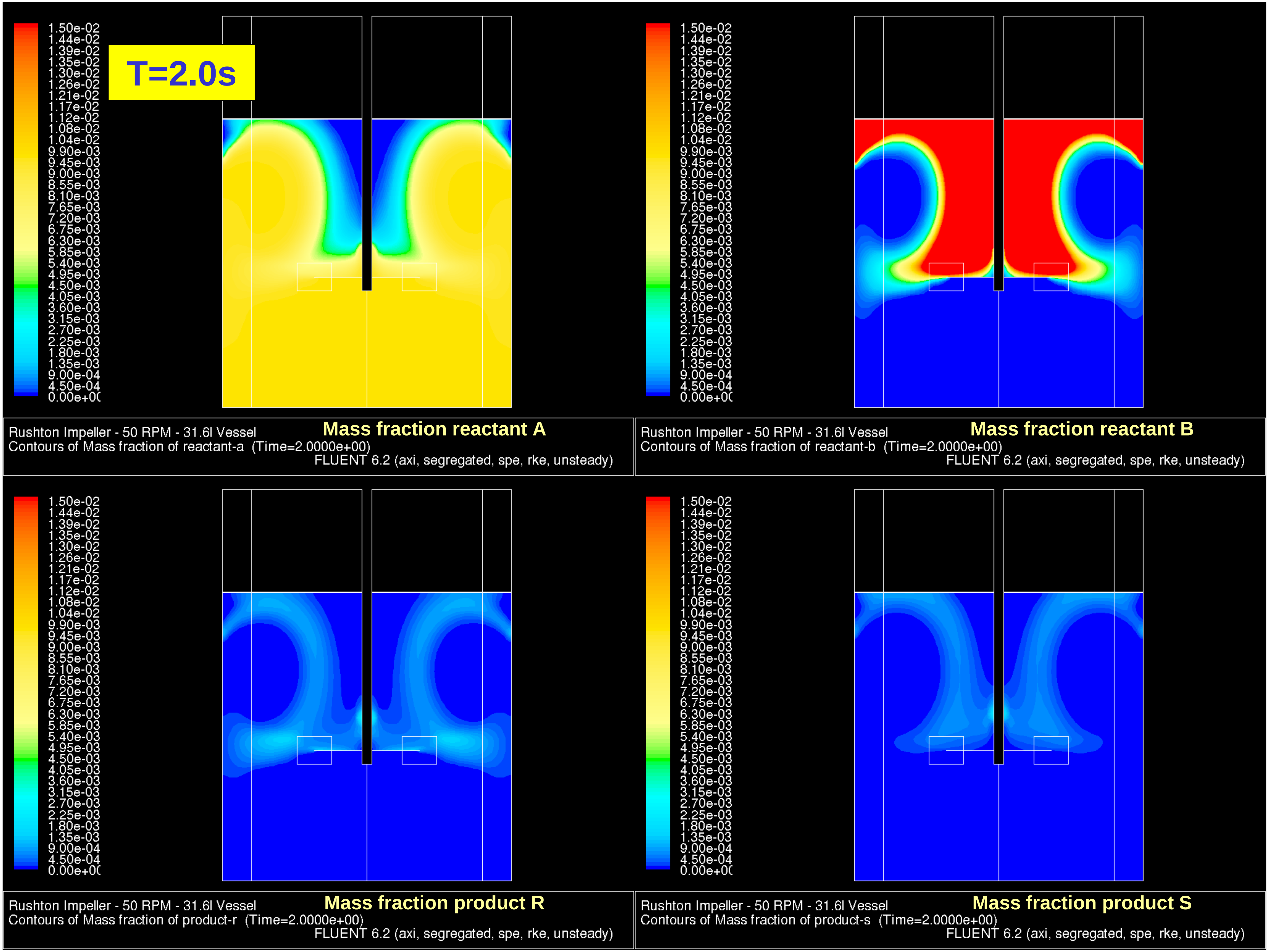
1.50e-03
1.20e-03
9.00e-04
6.00e-04
3.00e-04
0.00e+0
T=0s
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Rate of Reaction-1 (kgmol/m3-s)
Reaction rate 1: A + B → R
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Rate of Reaction- 2 (kgmol/m3-s)
Reaction rate 2: B + R → S
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
T=0.4s
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Rate of Reaction-1 (kgmol/m3-s) (Time=4.0000e-01)
Reaction rate 1: A + B → R
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Rate of Reaction-2 (kgmol/m3-s) (Time=4.0000e-01)
Reaction rate 2: B + R → S
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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1.08e-02
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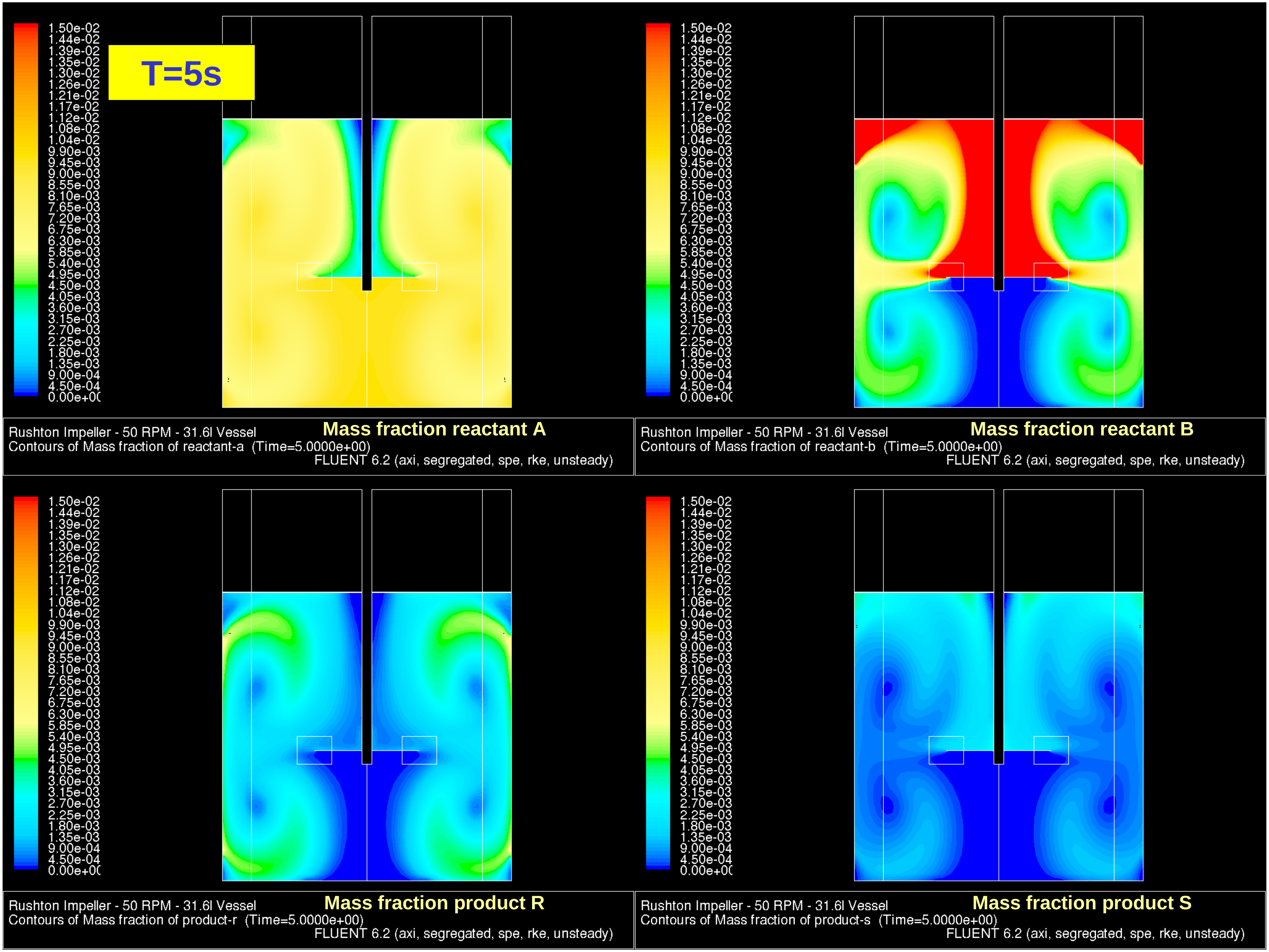
2.25e-03
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant A
Contours of Mass fraction of reactant-a (Time=2.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant B
Contours of Mass fraction of reactant-b (Time=2.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product R
Contours of Mass fraction of product-r (Time=2.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product S
Contours of Mass fraction of product-s (Time=2.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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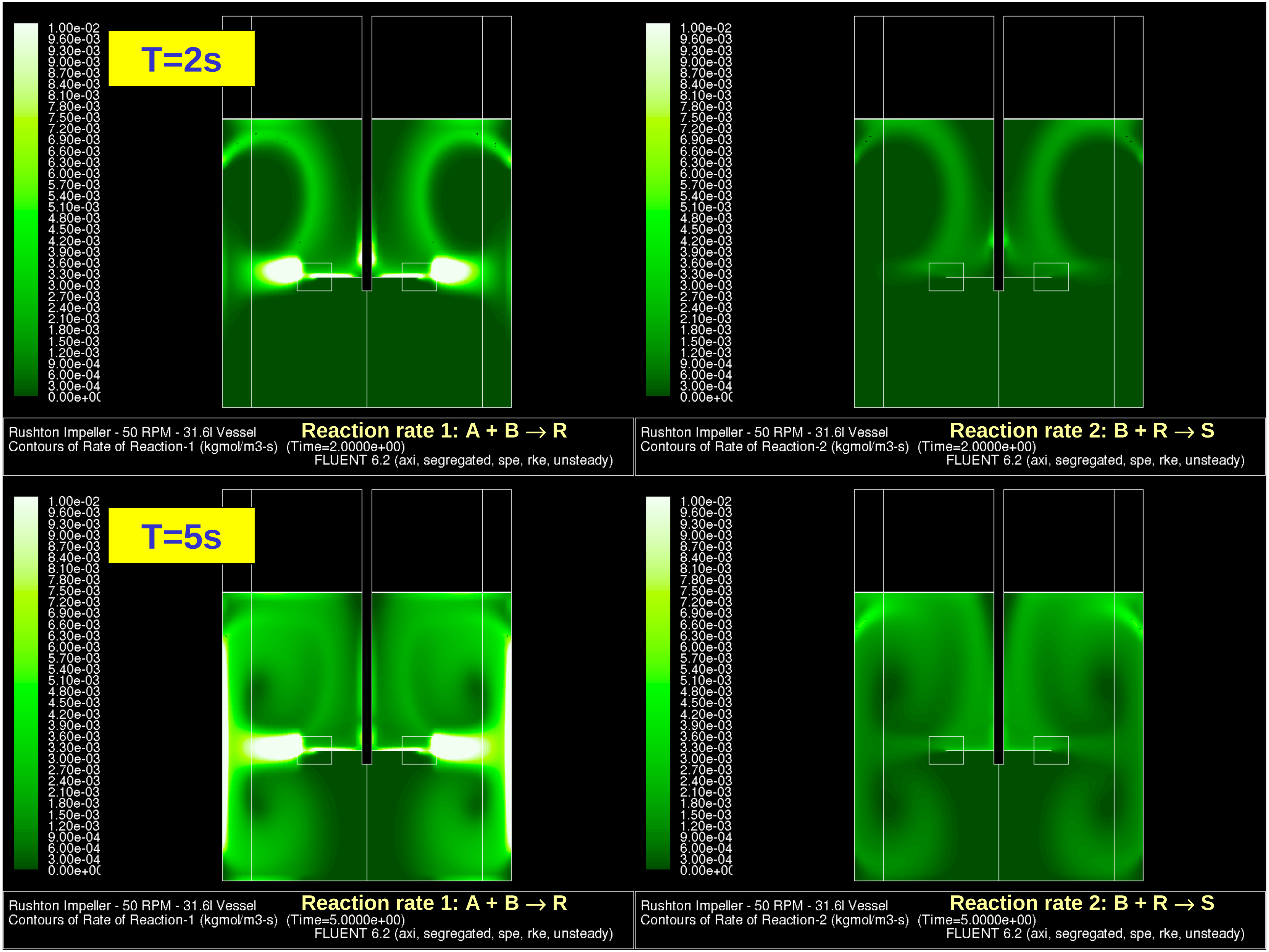
Mass fraction reactant A
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of reactant-a (Time=5.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Mass fraction reactant B
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of reactant-b (Time=5.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Mass fraction product R
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of product-r (Time=5.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Mass fraction product S
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of product-s (Time=5.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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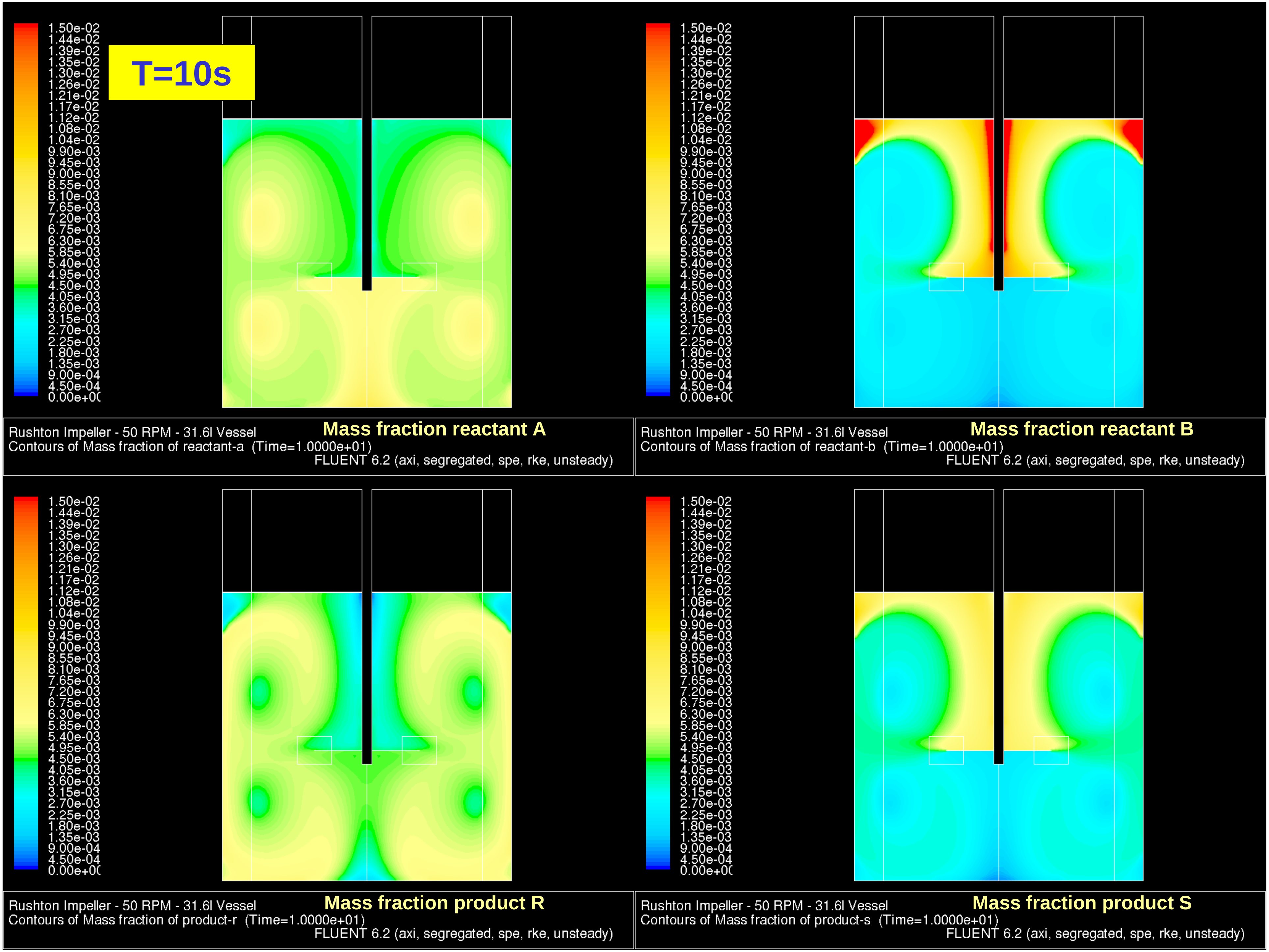
1.20e-03
9.00e-04
6.00e-04
3.00e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 1: A + B → R
Contours of Rate of Reaction-1 (kgmol/m3-s) (Time=2.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 2: B + R → S
Contours of Rate of Reaction-2 (kgmol/m3-s) (Time=2.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
T=5s
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 1: A + B → R
Contours of Rate of Reaction-1 (kgmol/m3-s) (Time=5.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 2: B + R → S
Contours of Rate of Reaction-2 (kgmol/m3-s) (Time=5.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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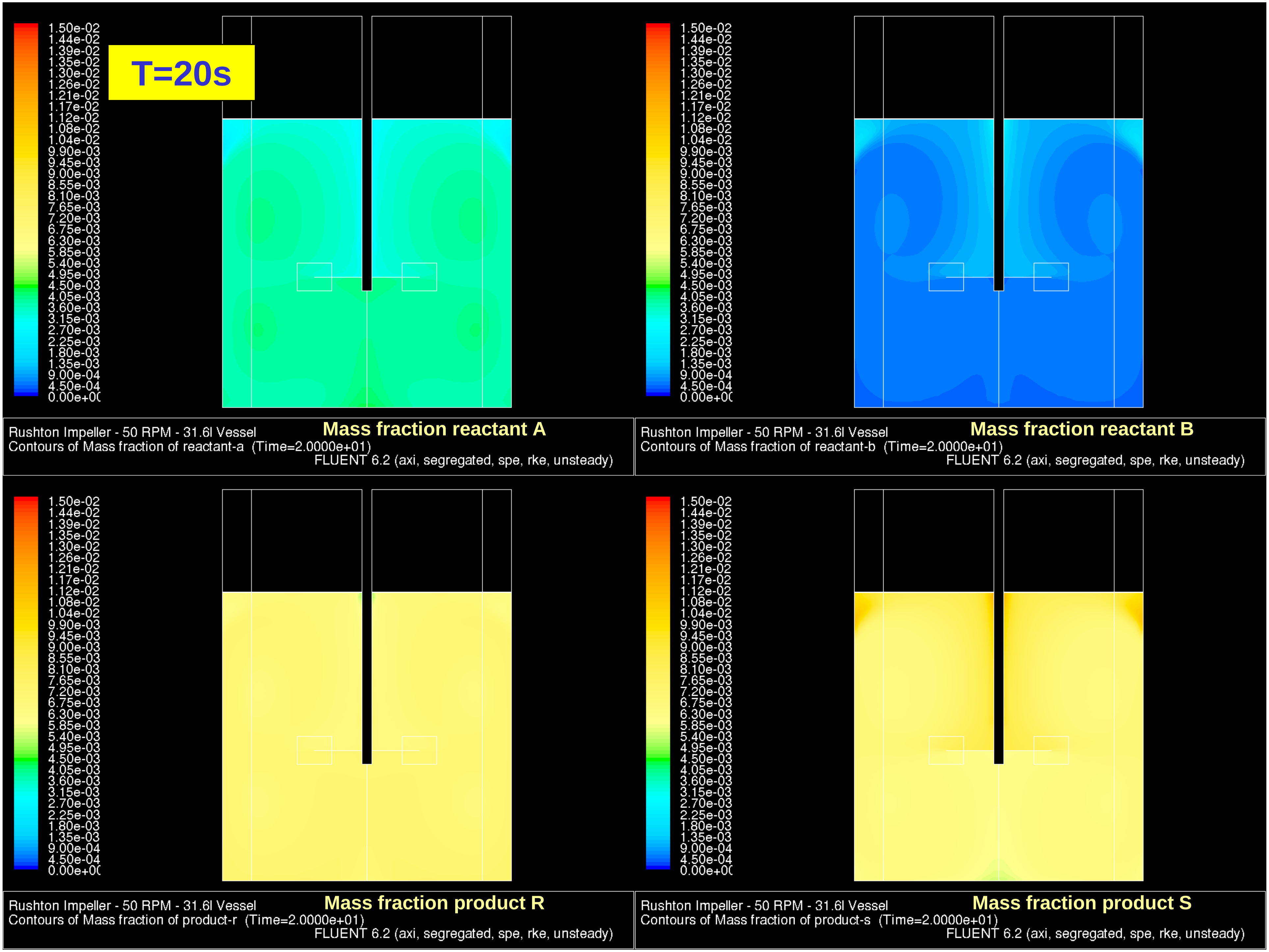
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+0
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant A
Contours of Mass fraction of reactant-a (Time=1.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant B
Contours of Mass fraction of reactant-b (Time=1.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product R
Contours of Mass fraction of product-r (Time=1.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product S
Contours of Mass fraction of product-s (Time=1.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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3.15e-03
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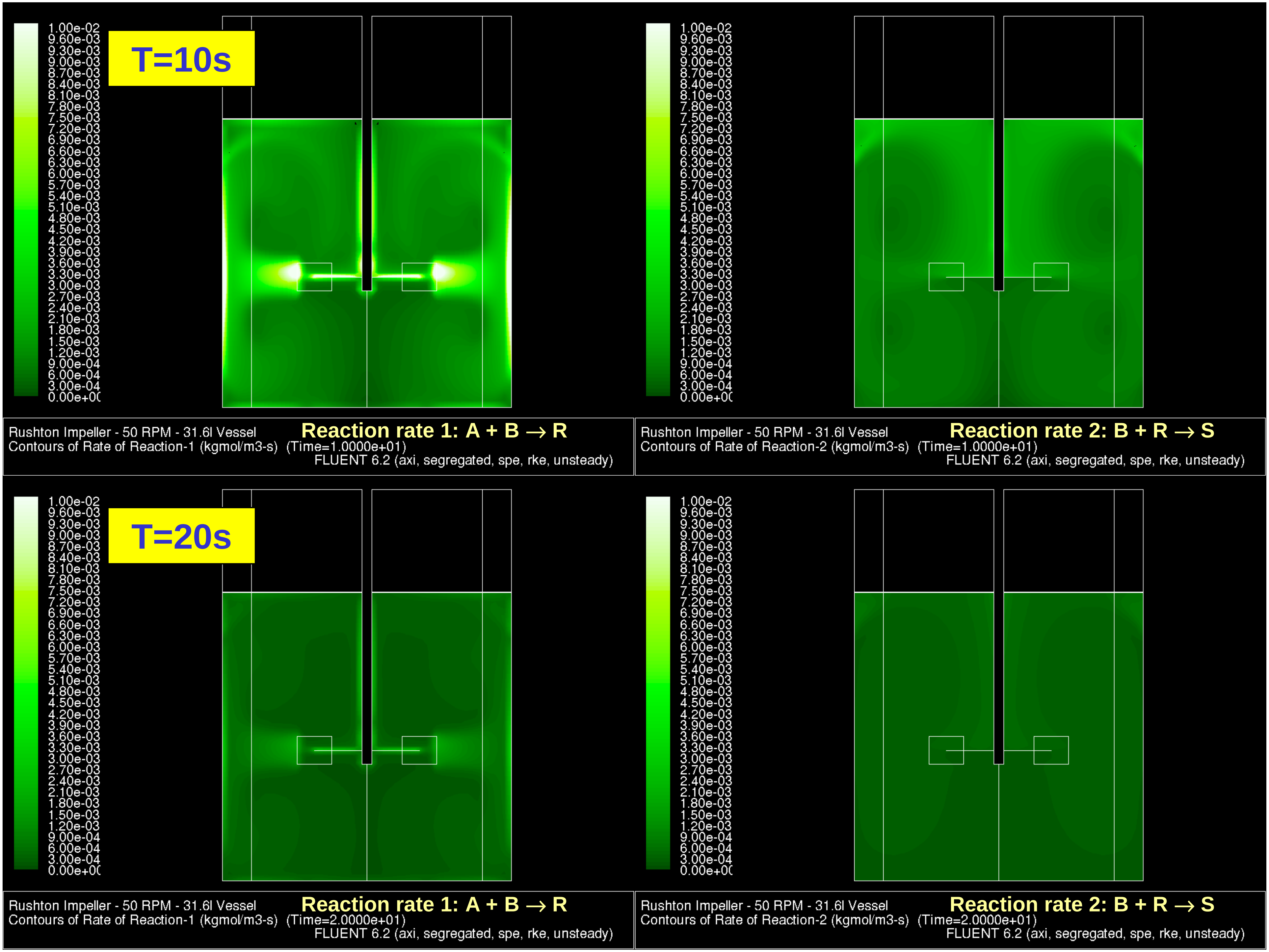
2.25e-03
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant A
Contours of Mass fraction of reactant-a (Time=2.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant B
Contours of Mass fraction of reactant-b (Time=2.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product R
Contours of Mass fraction of product-r (Time=2.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product S
Contours of Mass fraction of product-s (Time=2.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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1.50e-03
1.20e-03
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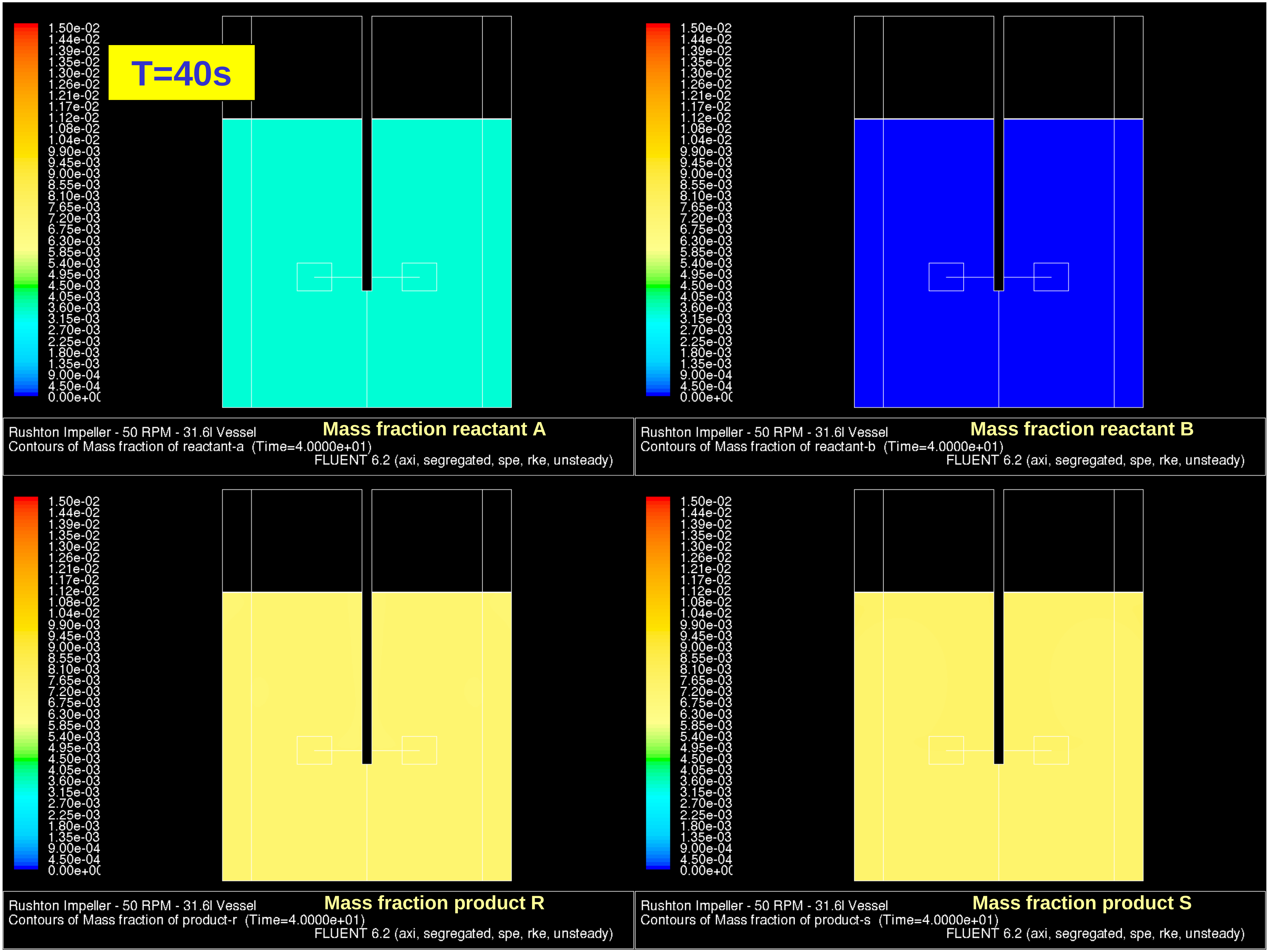
6.00e-04
3.00e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 1: A + B → R
Contours of Rate of Reaction-1 (kgmol/m3-s) (Time=1.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 2: B + R → S
Contours of Rate of Reaction-2 (kgmol/m3-s) (Time=1.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
T=20s
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 1: A + B → R
Contours of Rate of Reaction-1 (kgmol/m3-s) (Time=2.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Reaction rate 2: B + R → S
Contours of Rate of Reaction-2 (kgmol/m3-s) (Time=2.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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1.04e-02
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8.10e-03
7.65e-03
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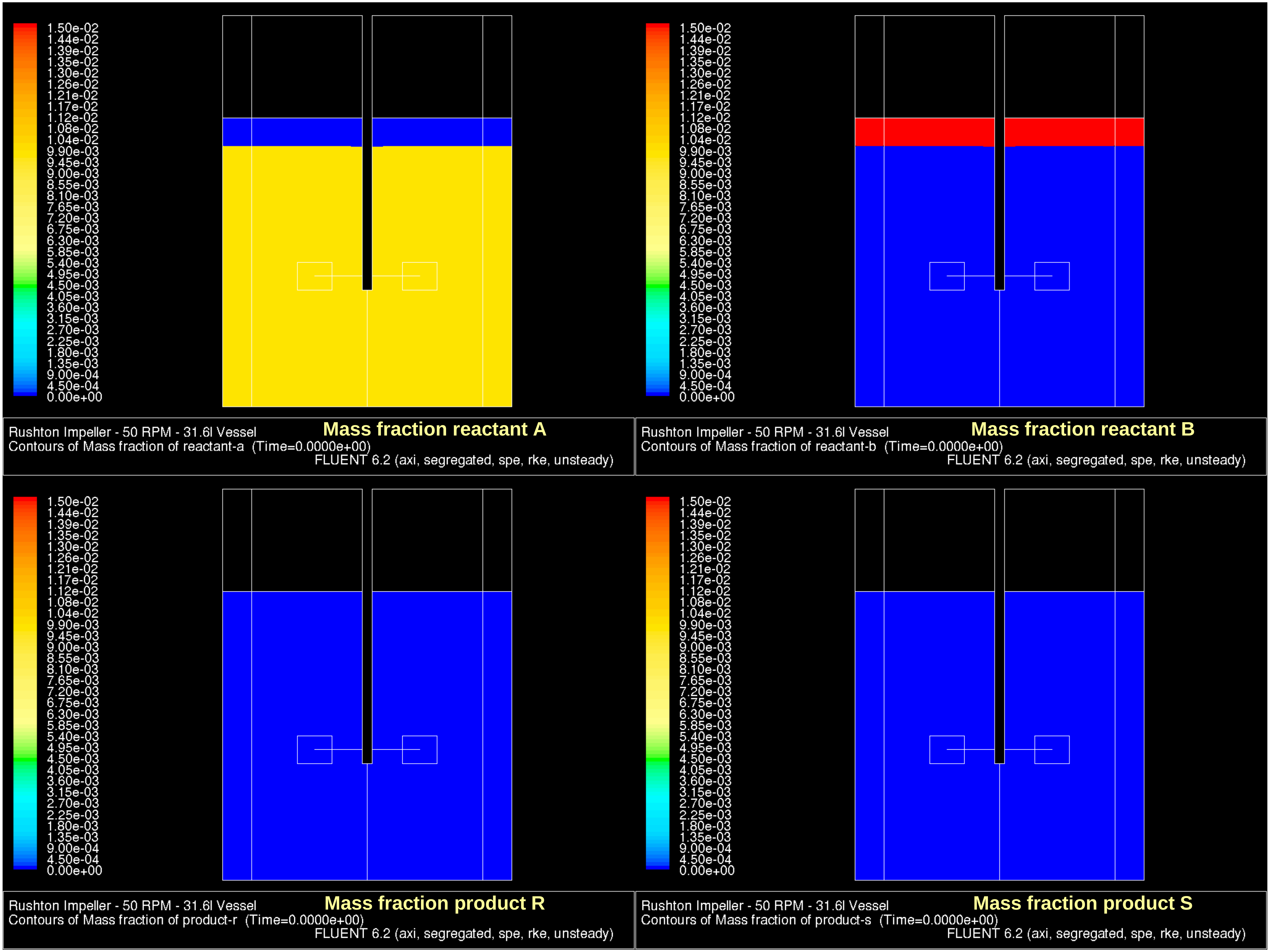
3.15e-03
2.70e-03
2.25e-03
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant A
Contours of Mass fraction of reactant-a (Time=4.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant B
Contours of Mass fraction of reactant-b (Time=4.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product R
Contours of Mass fraction of product-r (Time=4.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product S
Contours of Mass fraction of product-s (Time=4.0000e+01)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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1.04e-02
9.90e-03
9.45e-03
9.00e-03
8.55e-03
8.10e-03
7.65e-03
7.20e-03
6.75e-03
6.30e-03
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5.40e-03
4.95e-03
4.50e-03
4.05e-03
3.60e-03
3.15e-03
2.70e-03
2.25e-03
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant A
Contours of Mass fraction of reactant-a (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
1.50e-02
1.44e-02
1.39e-02
1.35e-02
1.30e-02
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1.04e-02
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9.00e-03
8.55e-03
8.10e-03
7.65e-03
7.20e-03
6.75e-03
6.30e-03
5.85e-03
5.40e-03
4.95e-03
4.50e-03
4.05e-03
3.60e-03
3.15e-03
2.70e-03
2.25e-03
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction reactant B
Contours of Mass fraction of reactant-b (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
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1.30e-02
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3.15e-03
2.70e-03
2.25e-03
1.80e-03
1.35e-03
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4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product R
Contours of Mass fraction of product-r (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)
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1.39e-02
1.35e-02
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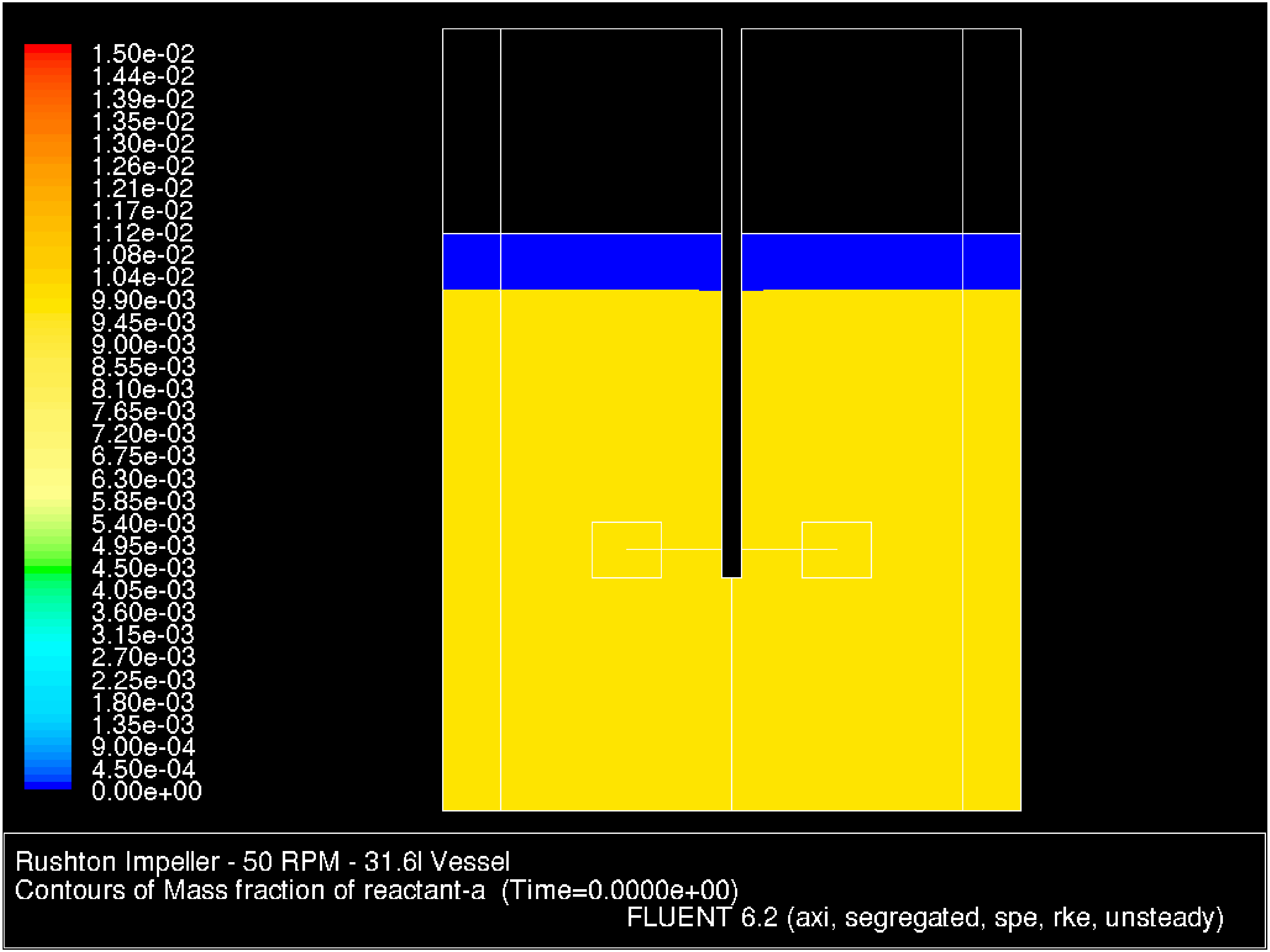
3.60e-03
3.15e-03
2.70e-03
2.25e-03
1.80e-03
1.35e-03
9.00e-04
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Mass fraction product S
Contours of Mass fraction of product-s (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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7.65e-03
7.20e-03
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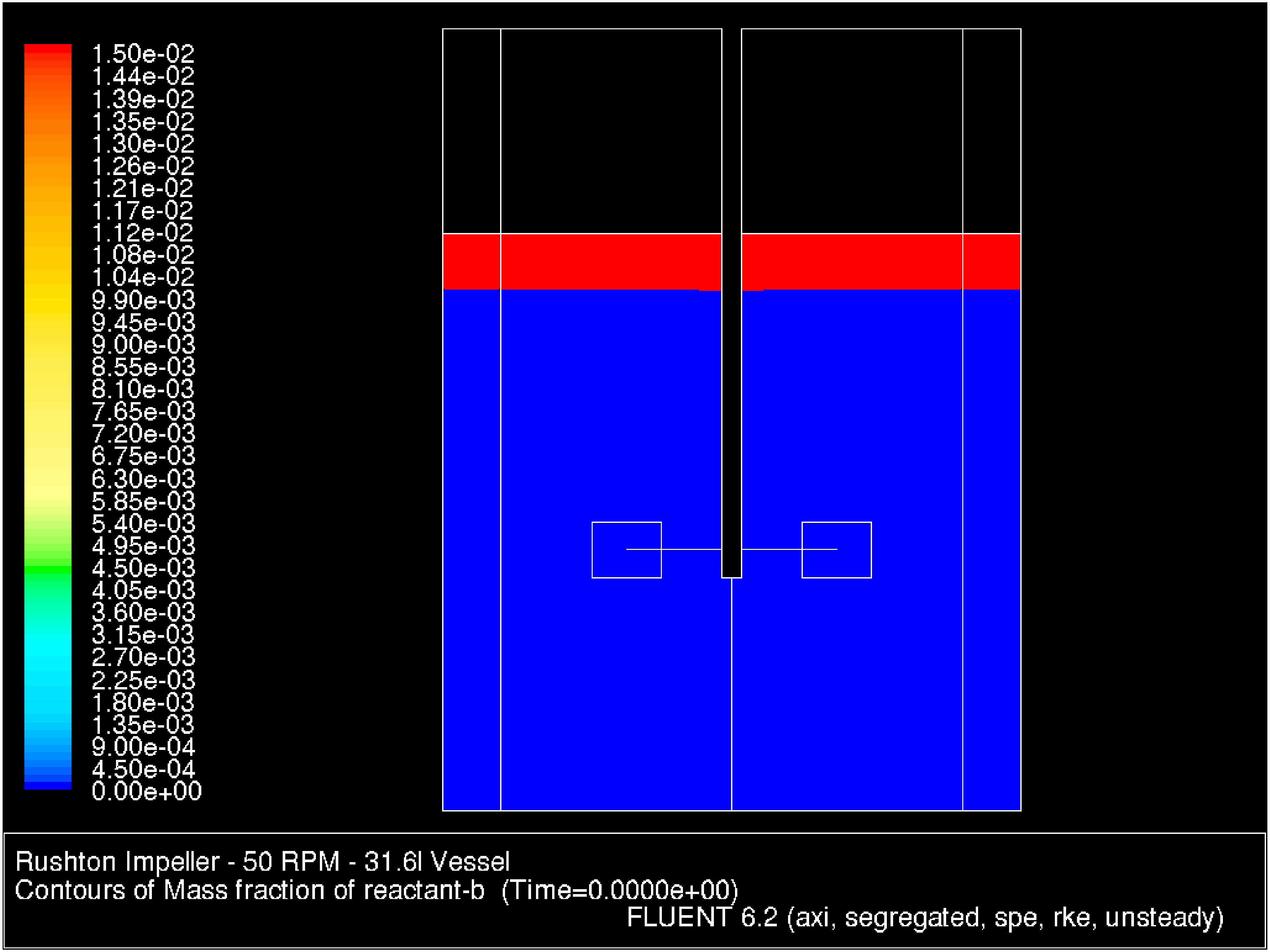
4.50e-04
0.00e+00
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of reactant-a (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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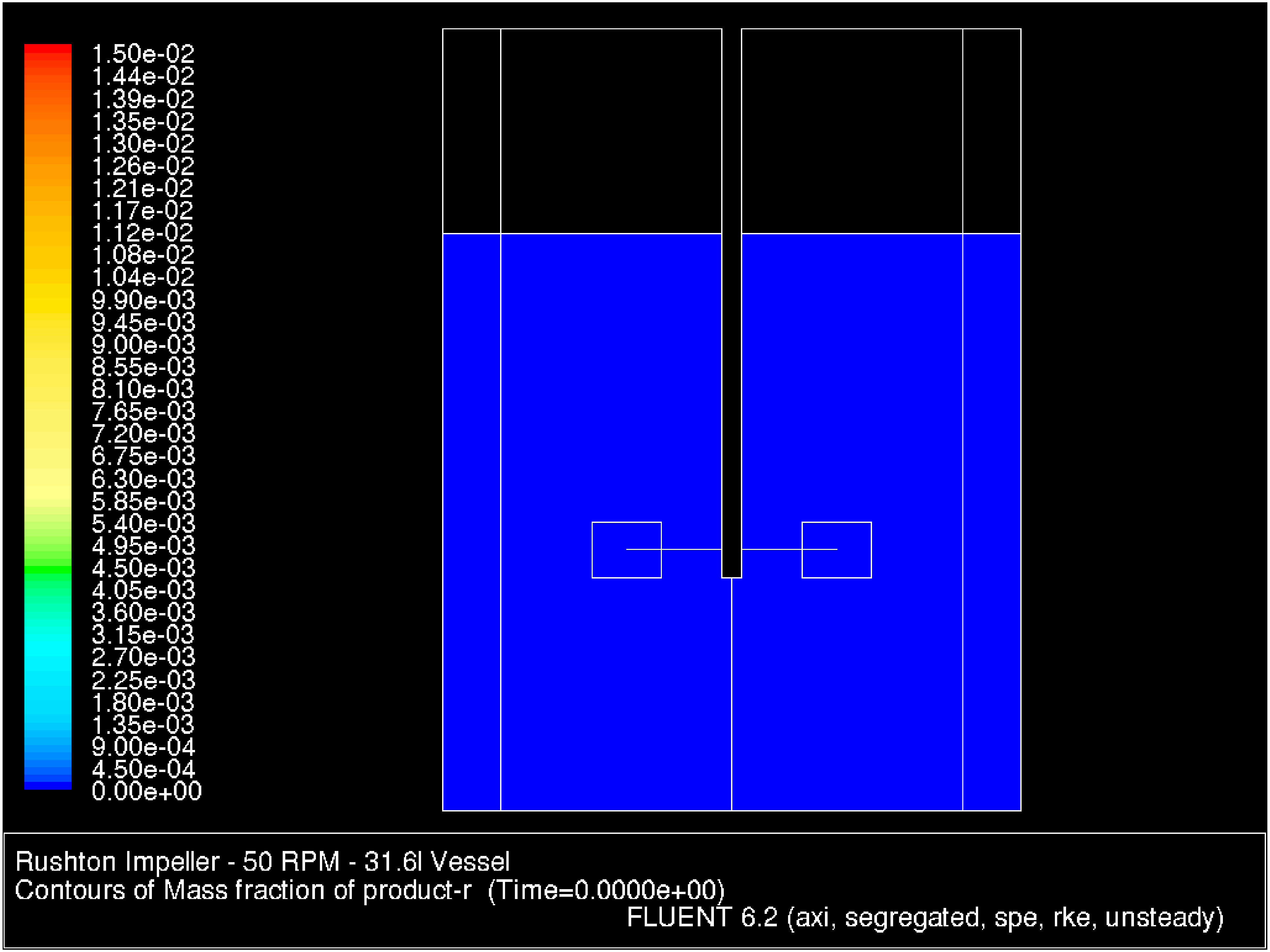
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of reactant-b (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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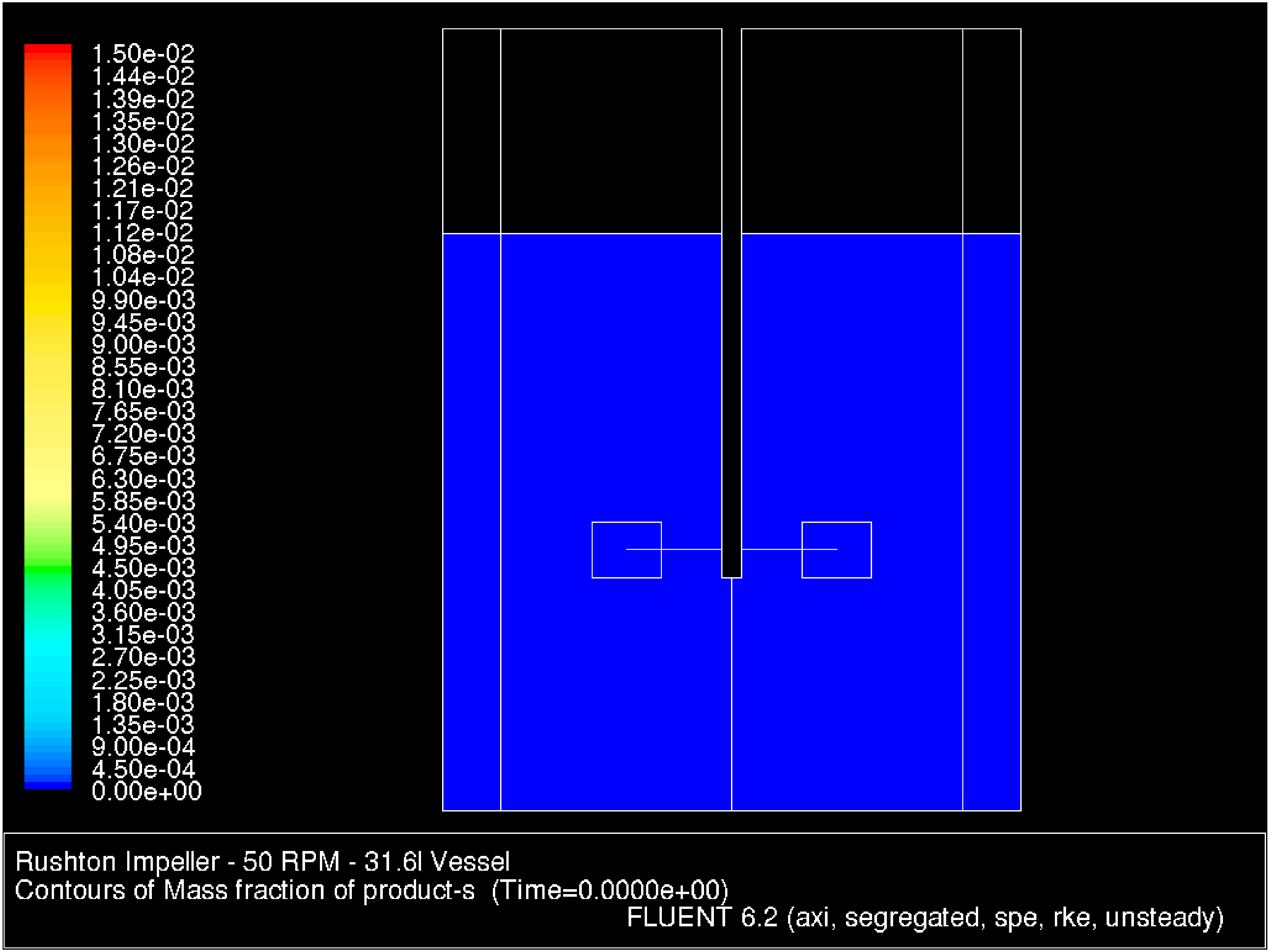
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of product-r (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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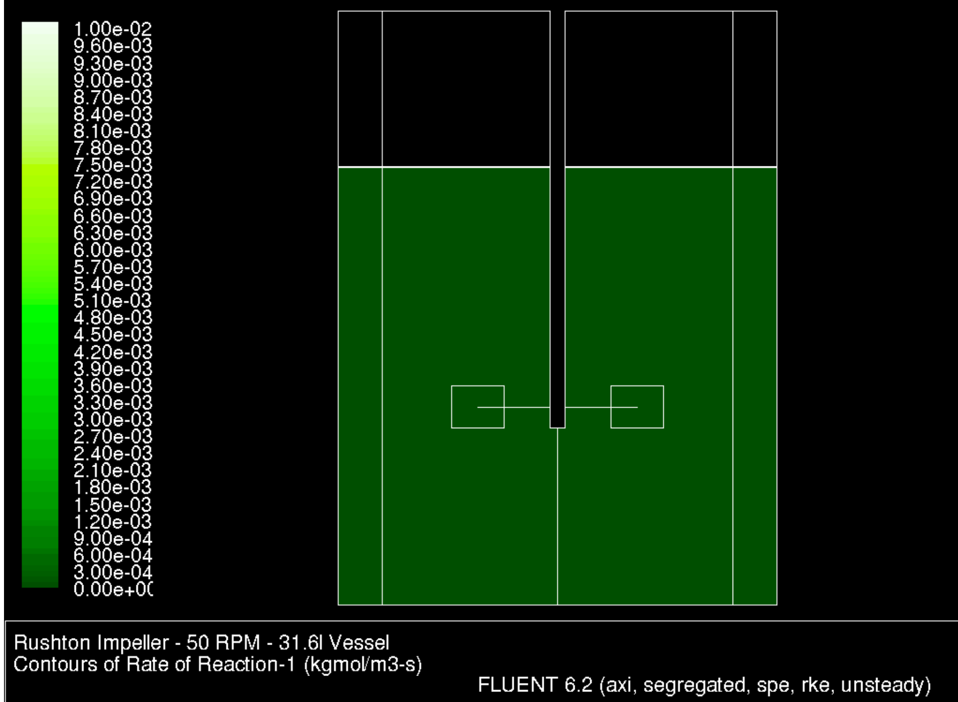
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Mass fraction of product-s (Time=0.0000e+00)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)

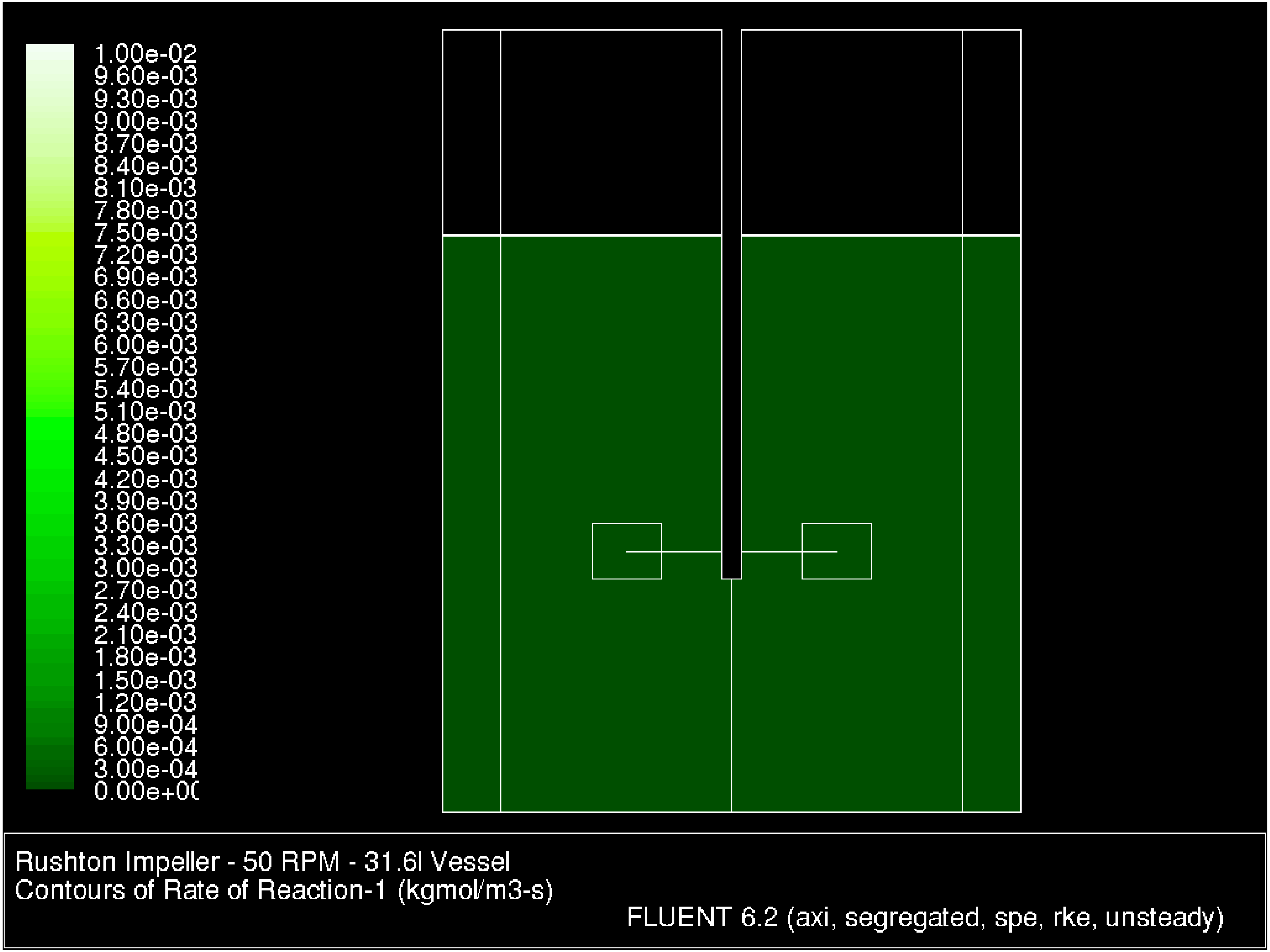


Reaction rate 1

$A + B \rightarrow R$

Reaction rate 2

$B + R \rightarrow S$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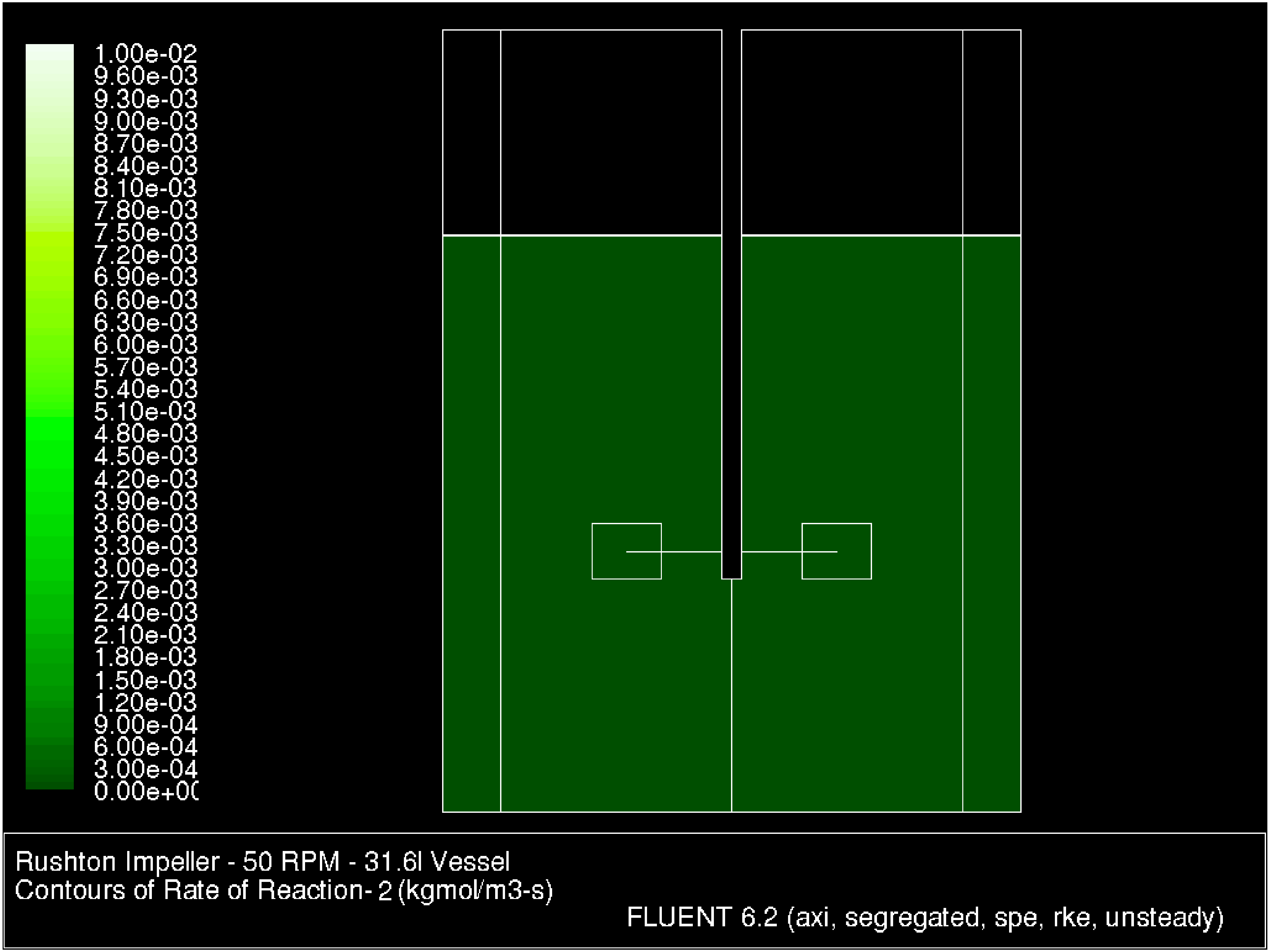
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Rate of Reaction-1 (kgmol/m3-s)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)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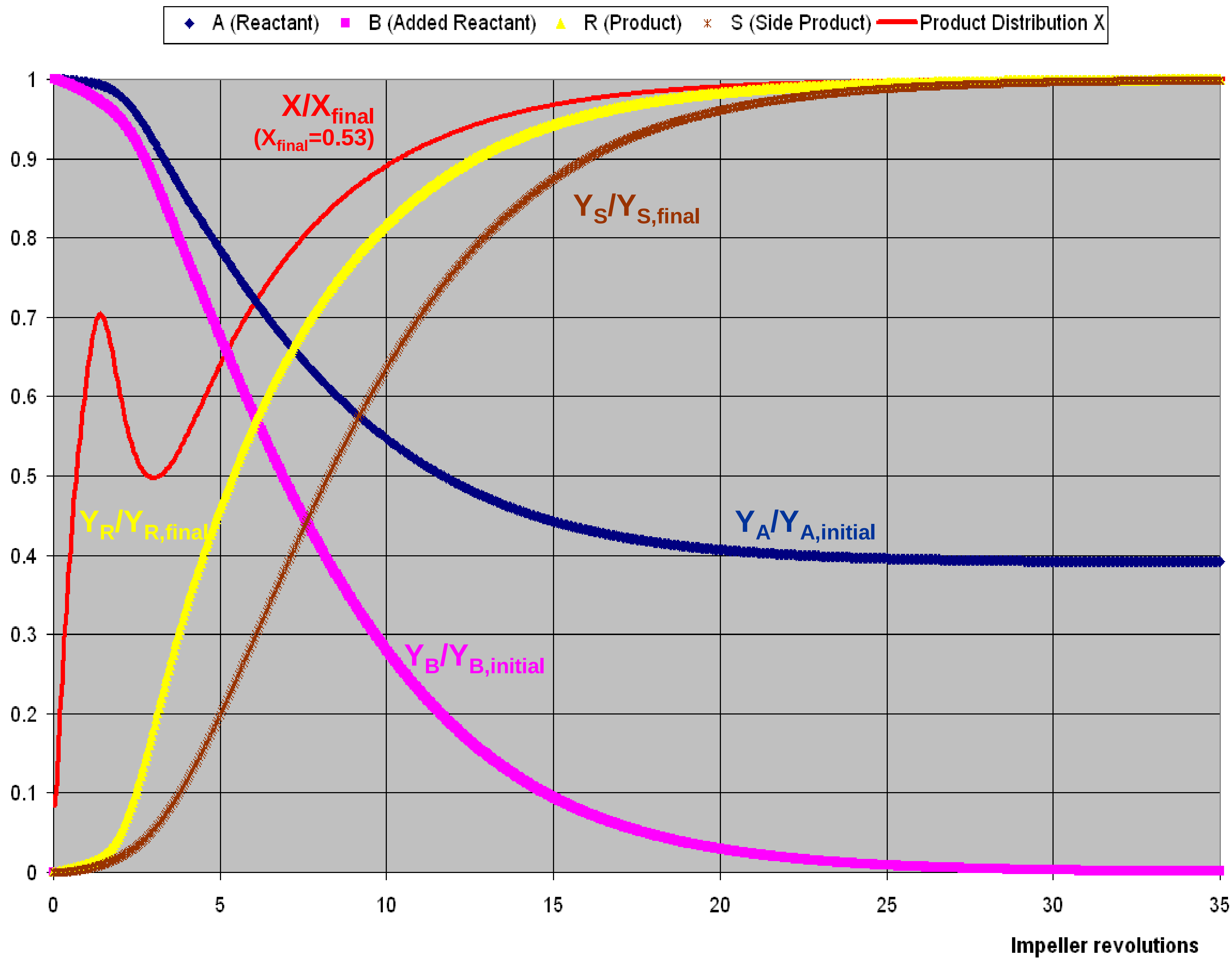
Rushton Impeller - 50 RPM - 31.6l Vessel
Contours of Rate of Reaction- 2 (kgmol/m3-s)
FLUENT 6.2 (axi, segregated, spe, rke, unsteady)



A (Reactant)
B (Added Reactant)
R (Product)
S (Side Product)
Product Distribution X
X/X_{final}
(X_{final}=0.53)
Y_S/Y_{S,final}
Y_R/Y_{R,final}
Y_A/Y_{A,initial}
Y_B/Y_{B,initial}
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
35
Impeller revolutions

Other models

- The eddy-dissipation-concept (EDC) model.
  - This is an extension of the eddy-dissipation model to finite rate chemistry; proposed by Gran and Magnussen (1996).
  - Equations are very different, however. Assumes reactions occur on small scales and calculates a volume fraction of small scale eddies in which the reactions occur.
  - It is more suitable for more complex reaction sets than the finite-rate/eddy-dissipation model and requires less user tuning. It is computationally expensive, however.
- Dedicated combustion models:
  - Pre-mixed combustion models.
  - Non pre-mixed combustion models.
  - Partially pre-mixed combustion models.
  - Finite-rate kinetics in turbulent flames (composition PDF transport model).
- Not standard in FLUENT: reactions for which the kinetics can not practically be described by Arrhenius rate style kinetics. Such kinetics needs to be added through user defined source terms. Examples:
  - Fermentation kinetics.
  - Polymerization.

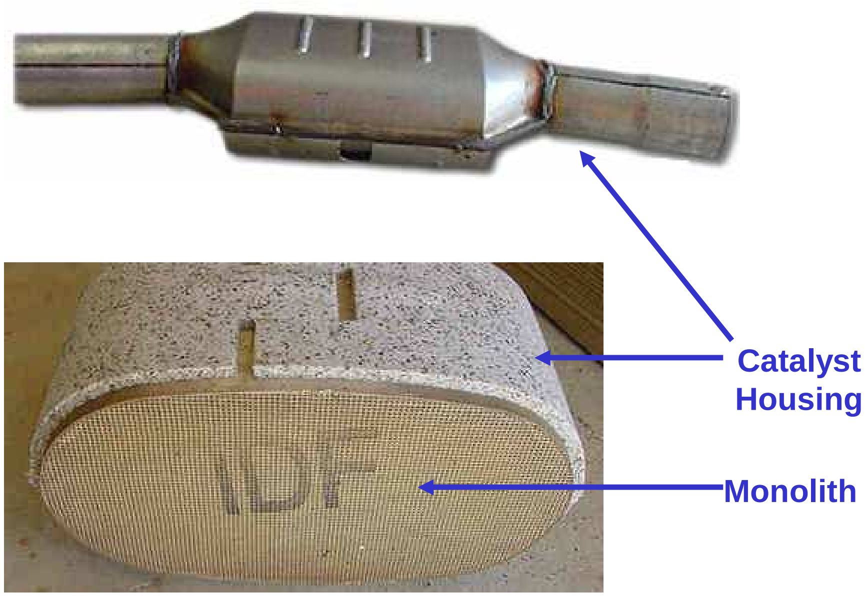
Complex reaction sets

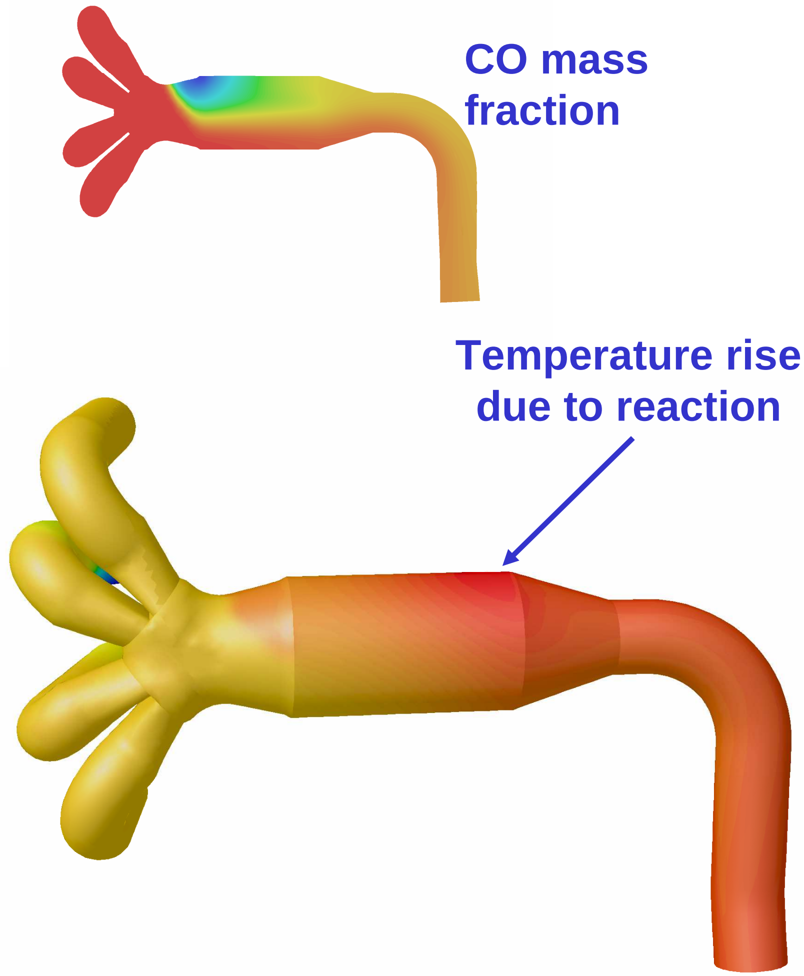
- Many real life systems have complex sets of reactions, often many hundreds.
- Not all reactions may be known in detail, and there may be uncertainty in the rate constants.
- Large differences in time constants may make the reaction set hard (“stiff”) to solve.

$\Longrightarrow$ The reaction sets modeled are usually simplifications of what happens in real life.

Example: catalytic converter

- The main component of the catalytic converter is the monolith
- The monolith usually has a honeycomb structure, which is coated with one or more catalysts, known as the washcoat (platinum, rhodium, palladium).





Reaction mechanism

61 surface reactions
8 gas phase species
23 surface site species
2 catalysts

C_3H_6 oxidation on Pt

Adsorption

O_2 + Pt(S) + Pt(S) → O(S) + O(S)
C_3H_6 + Pt(S) + Pt(S) → C_3H_6(S)
C_3H_6 + O(S) + Pt(S) → C_3H_5(S) + OH(s)
H_2 + Pt(S) + Pt(S) → H(S) + H(S)
H_2O + Pt(S) → H_2O(S)
CO_2 + Pt(S) → CO_2(S)
CO + Pt(S) → CO(S)

Desorption

O(S) + O(S) → Pt(S) + Pt(S) +O_2
C_3H_6(S) → C_3H_6 + Pt(S) + Pt(S)
C_3H_5(s) + OH(s) → C_3H_6 + O(S) + Pt(S)
H(S) + H(S) → H_2 + Pt(S) + Pt(S)
H_2O(S) → Pt(S) + H_2O
CO(S) → CO + Pt(S)
CO_2 (S) → CO_2 + Pt(S)

Surface reactions

C_3H_5(S) + 5O(s)→5OH(S) + 3C(S)

C_3H_6(S) → C_3H_5(S) + H(S)
C_3H_5(S) + H(S) → C_3H_6(S)
C_3H_5(S) + Pt(S) → C_2H_3(S) + CH_2 (S)
C_2H_3(S) + CH_2(S) → C_3H_5(S) + Pt(S)
C_2H_3(S) + Pt(S) → CH_3(S) +C(S)
CH_3(S) + C(S) → C_2H_3(S) + Pt(S)

CH_3(S) + Pt(S) → CH_2(S) + H(S)
CH_2(S) + H(S) → CH_3(S) + Pt(S)
CH_2(S) + Pt(S) → CH(S) + H(S)
CH(S) + H(S) → CH_2(S) + Pt(S)
CH(s) + Pt(s) → C(S) + H(S)
C(S) + H(S) → CH(S) + Pt(S)

C_2H_3(S) + O(s) → Pt(S) + CH_3CO(S)
CH_3CO(S) + Pt(s) → C_2H_3(S) + CO(S)
CH_3(s) + CO(s) → Pt(S) + CH_3CO(S)
CH_3CO(s) + Pt(s) → CH_3(S) + CO(s)

CH_3(S) + OH(S) → CH_2(S) + H_2O(S)
CH_2(S) + H_2O(S) → CH_3(S)+ OH(S)
CH_2(S) + OH(S) → CH(S) + H_2O(S)
CH(S) + H_2O(S) → CH_2(S) + OH(S)
CH(S) + OH(S) → C(S) + H_2O(S)
C(S) + H_2O(S) → CH(S) + OH(S)

O(S) + H(S) → OH(S) + Pt(S)
OH(S) + Pt(S) → O(S) + H(S)
H(S) + OH(S) → H_2O(S) + Pt(S)
H_2O(S) + Pt(S) → H(S) + OH(S)
OH(S) + OH(S) → H_2O(S) + O(S)
H_2O(S) + O(S) → OH(S) + OH(S)

CO(S) + O(S) → CO_2 (S) + Pt(S)
CO_2 (S) + Pt(S) → CO(S) + O(S)
C(S) + O(S) → CO(S) + Pt(S)
CO(S) + Pt(S) → C(S) + O(S)

NO reduction on Pt

Adsorption
NO + Pt(s) → NO(S)

Desorption
NO(s) → NO + Pt(s)
N(s) + N(s) → N2 + Pt(s) +Pt(s)

Surface reactions
NO(S) + Pt(S) → N(S) + O(S)
N(S) + O(S) → NO(S) + Pt(S)

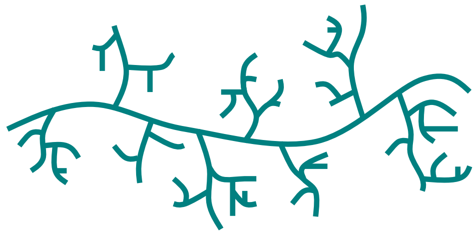
NO reduction & CO oxidation on Rh

Adsorption
O_2 + Rh(S) + Rh(S) → O(Rh) + O(Rh)
CO + Rh(S) → CO(Rh)
NO + Rh(S) → NO(Rh)

Desorption
O(Rh) + O(Rh) → O_2 + Rh(s) + Rh(S)
CO(Rh) → CO + Rh(S)
NO(Rh) → NO + Rh(S)
N(Rh)+ N(Rh) → N_2 + Rh(S) + Rh(S)

NO/CO Surface reactions
CO(Rh) +O(Rh) → CO_2 + RH(s) + Rh(s)
NO(Rh) + Rh(S) → N(Rh) + O(Rh)

Example: polymerization



- Polymerization of ethylene C_2H_4 into low-density poly-ethylene (LDPE).
- LDPE is a plastic resin used to make consumer products such as cellophane wrap, diaper liners, and squeeze bottles.
- It is important to be able to predict the properties of the LDPE depending on the precise reaction conditions.
- The low density polyethylene process is a complex chain of reactions
  - It involves many steps and many radicals of different lengths.
  - It starts with a small amount of initiator mixing with a large amount of monomer (ethylene).
  - The final product is a polymer (polyethylene) of varying length and structure.

The multi-step polymerization process

Initiator decomposition	$I \xrightarrow{k_I} 2A$
Chain initiation	$A + M \xrightarrow{k_{II}} R_1$
Propagation	$R_x + M \xrightarrow{k_p} R_{x+1}$
Chain transfer to monomer	$R_x + M \xrightarrow{k_{trm}} P_x + R_1$
Disproportionation termination	$R_x + R_y \xrightarrow{k_{td}} P_x + P_y$
Combination termination	$R_x + R_y \xrightarrow{k_{tc}} P_{x+y}$

I = initiator **M = monomer** **P_x = polymer (length x)**

A = initiator radical **R_x = radical (length x)**

Solution method

- Instead of solving species equations for every possible radical or polymer length a mathematical method called the “method of moments” is used.
- Introduce moments of radical and dead polymer chains:

$$\lambda_0 = \sum_{x=1\to\infty} R_x \qquad \lambda_1 = \sum_{x=1\to\infty} xR_x \qquad \lambda_2 = \sum_{x=1\to\infty} x^2 R_x$$

$$\mu_0 = \sum_{x=1\to\infty} P_x \qquad \mu_1 = \sum_{x=1\to\infty} xP_x \qquad \mu_2 = \sum_{x=1\to\infty} x^2 P_x$$

- Here R_x and P_x are the mole fractions of radical and polymer with length x (measured in number of monomers per molecule) respectively.
- The moments are used to reduce the reaction set and compute the product characteristics, such as molecular weight distribution.
- Energy sources are added to represent the heat of the propagation reaction.
- The method of moments is used to derive the molecular weight distribution and polydispersity.
- Six additional scalar transport equations are solved for the moments of radicals and polymers.

Simplified polymerization process

1. $I \xrightarrow{k_I} 2A$	initiator decomposition
2. $A + M \xrightarrow{k_{II}} R$	chain initiation
3. $R + M \xrightarrow{k_p} R$	propagation
4. $R + R \xrightarrow{(k_{td}+k_{tc})/2} P$	termination
5. $M + (R) \xrightarrow{k_{trm}} P + (R)$	chain transfer to monomer

Obtaining the product characteristics

- Molecular weight:
  - Number averaged:

$$NWD = MW_m \frac{\mu_1}{\mu_0}$$

  - Mass averaged:

$$MWD = MW_m \frac{\mu_2}{\mu_1}$$

  - Here MW_m is the molecular weight of the monomer.

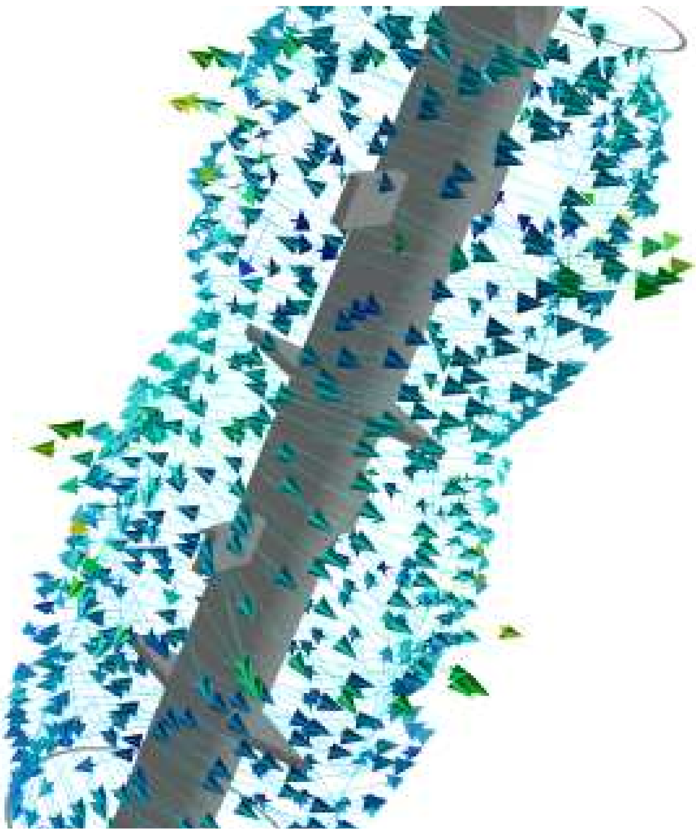
- Polydispersity Zp: this is the ratio of the mass average molecular weight to the number average molecular weight. It indicates the distribution of individual molecular weights in a batch of polymers.

$$Zp = \frac{\mu_0 \mu_2}{\mu_1^{\ 2}}$$

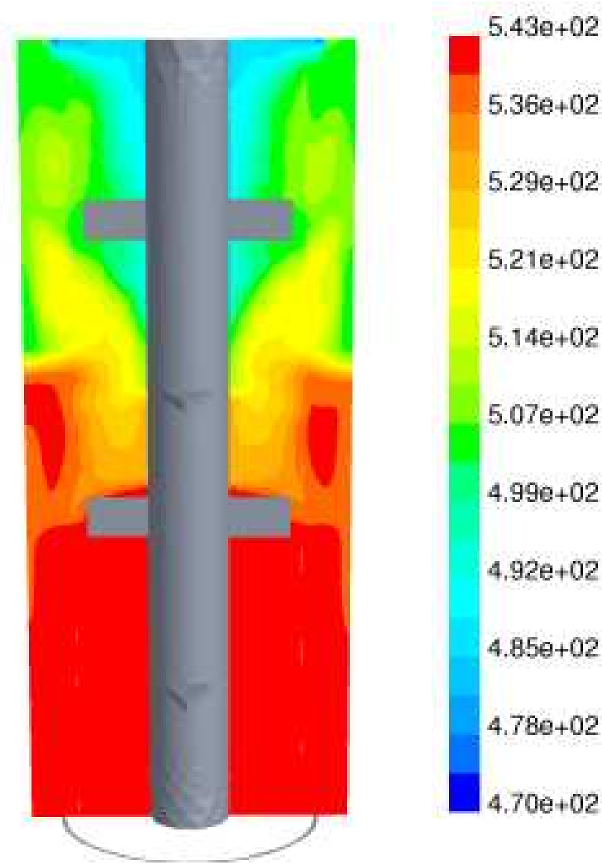
- Monomer conversion X. Here Y_M and $Y_{0,M}$ are the final and initial monomer mass fractions respectively.

$$X = 1 - \frac{Y_M}{Y_{0,M}}$$

Autoclave reactor results



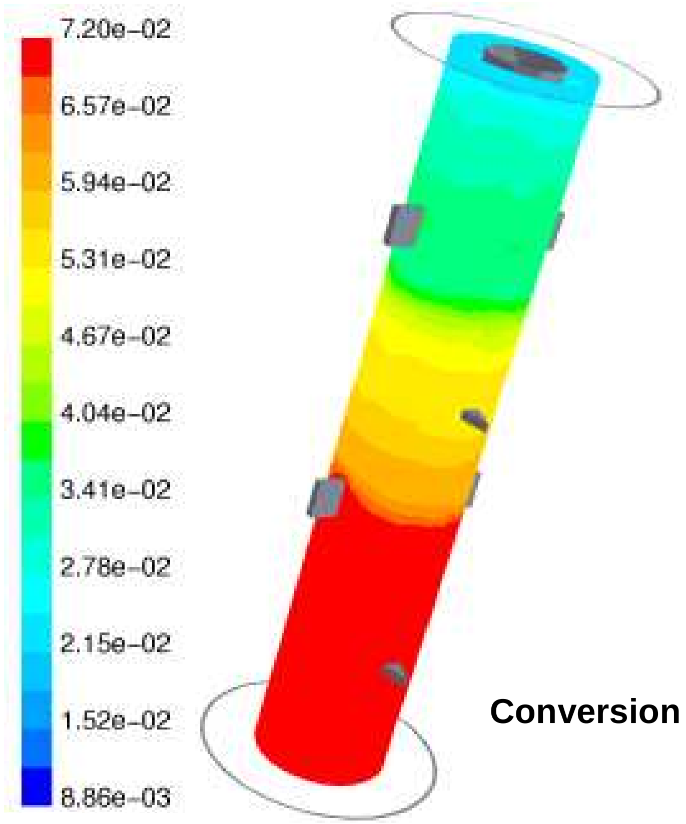
Velocity vectors

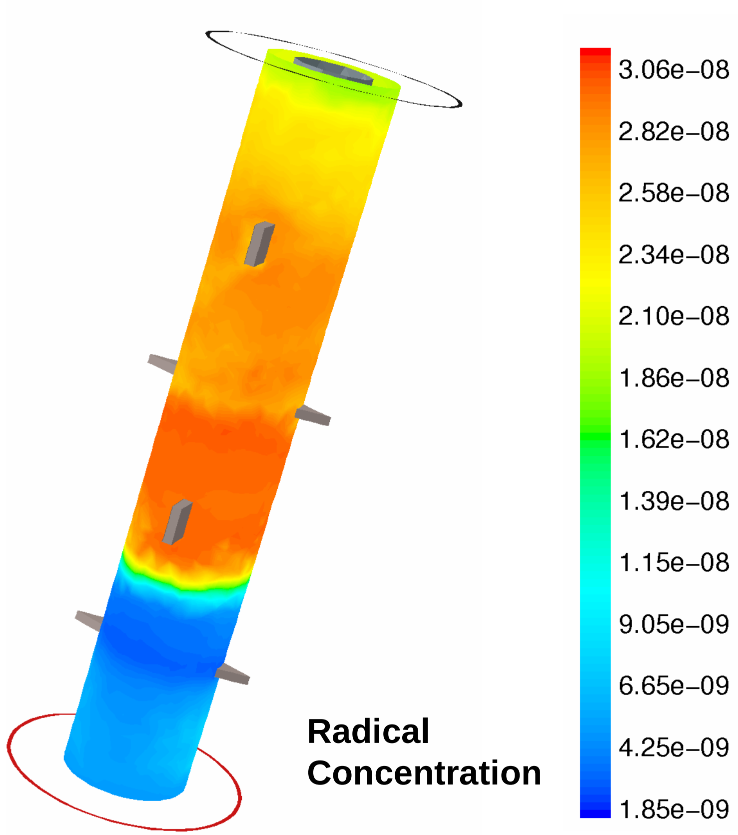


Temperature (K)

- ✓ **Strong swirling due to the lack of baffles**
- ✓ **Maximum temperatures above 610K would cause ethylene decomposition and thermal runaway**

Autoclave reactor results

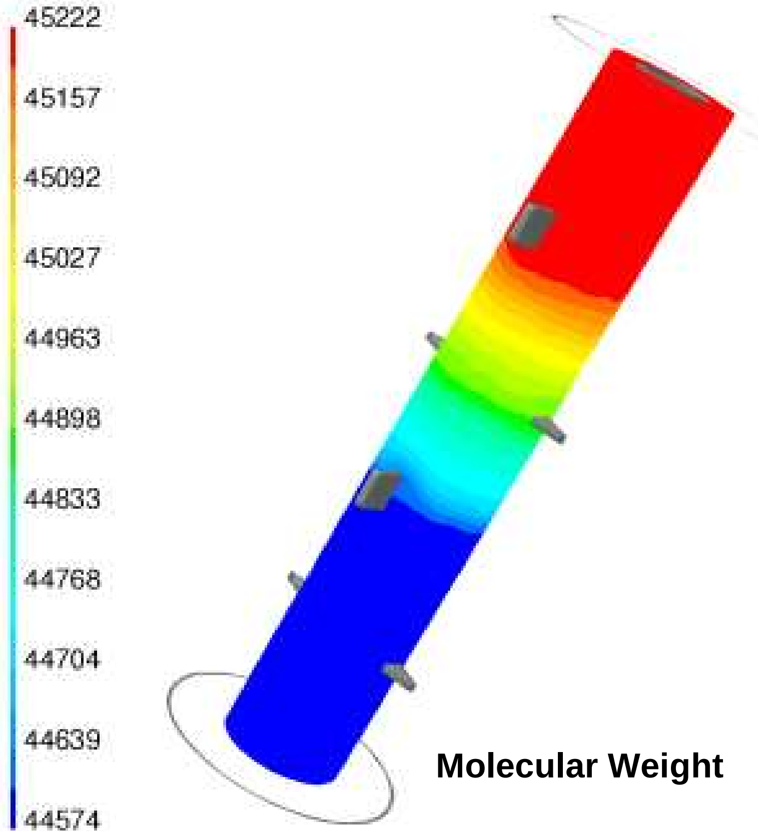


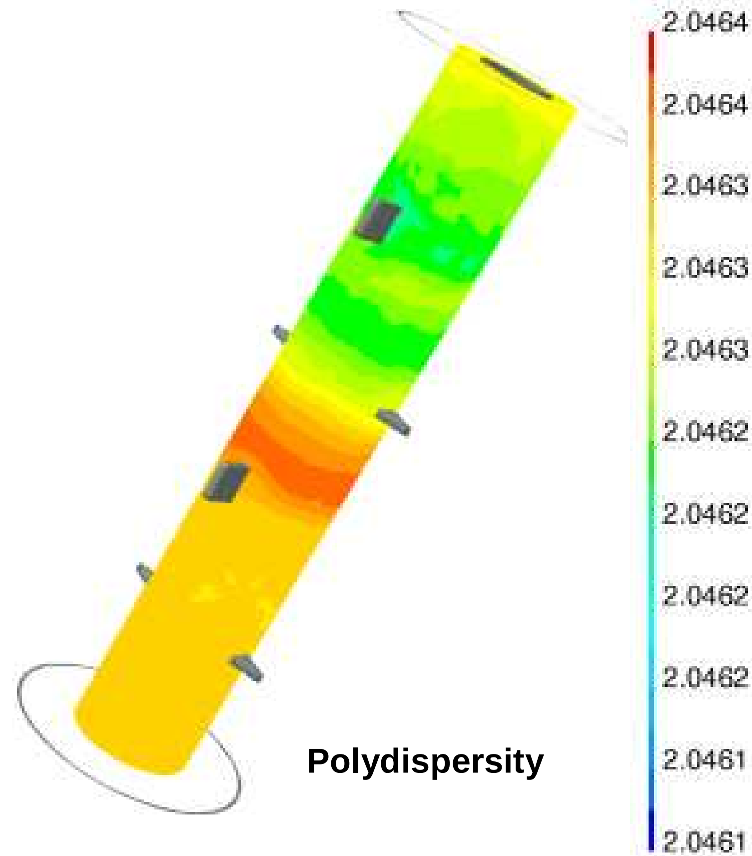


- ✓ **A 7.2% conversion achieved**
- ✓ **Conversion strongly depends on the inlet initiator concentration and inlet temperature**

- ✓ **Radicals are formed in the middle of the reactor by the initiation reaction and consumed to form polymer by the termination reaction**

Autoclave reactor results





- ✓ **Mass averaged molecular weights are from 44574 - 45222**
- ✓ **Polydispersity is about 2.046**
- ✓ **A uniform distribution indicates a high quality production of polymers**

Conclusion

- Modeling chemical reaction requires the definition of source terms.
- Reaction kinetics can usually be defined, but not in all systems does the reaction proceed at the kinetic rate.
- Mixing effects can be incorporated into using a variety of models, developed and optimized for particular systems.
- In many cases, one of the following will be necessary:
  - Simplification of the reaction set.
  - Determination of model constants.
  - Implementation of custom source terms or models.