Development of a Liquid Bridge Model for Particle Agglomeration and Defluidization in Plastic Pyrolysis

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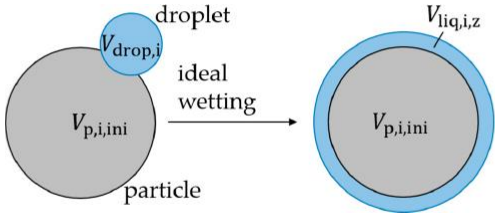
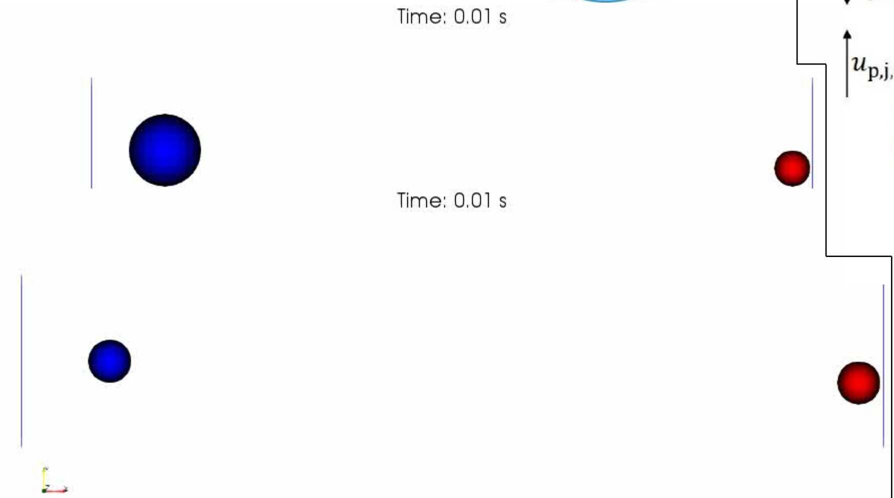
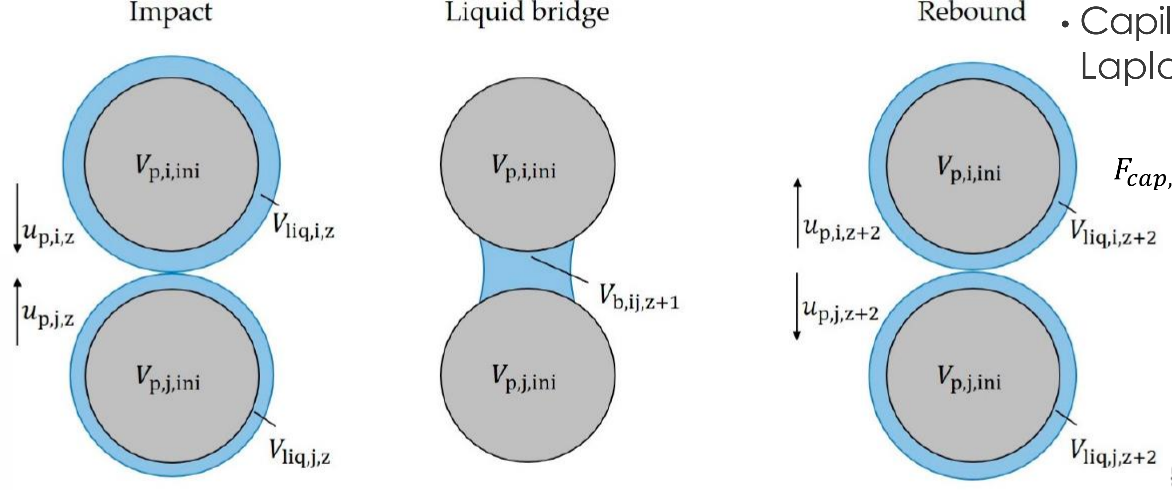
Liquid Layer Development Proof-of-Concept

- Molten plastic that forms during the pyrolysis of plastic or municipal solid waste feedstock can lead to particle agglomeration
- A proof-of-concept of a liquid bridge model is developed based on Grohn et al.[1] and verification studies are completed





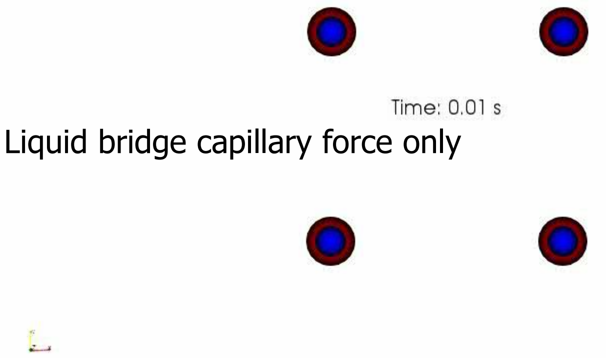
- Molten plastic droplet deleted on contact with sand particle and mass and species transferred in perfectly inelastic collision
- Conservation of mass and momentum verified numerically



$V_{b,ij,z+1} = V_{liq,i,z} + V_{liq,j,z}$

$V_{b,ij,z+1}/2 = V_{liq,i,z+2} = V_{liq,j,z+2}$

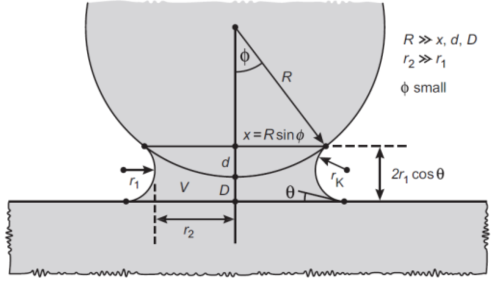
No liquid bridge

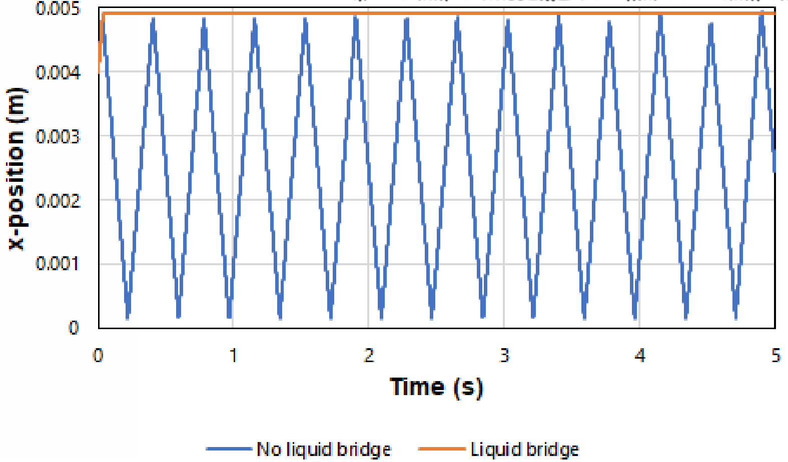


Liquid bridge capillary force only

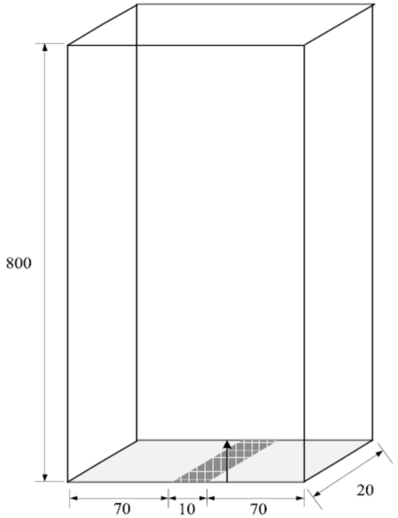
- Capillary forces are based on Laplace pressure[2]

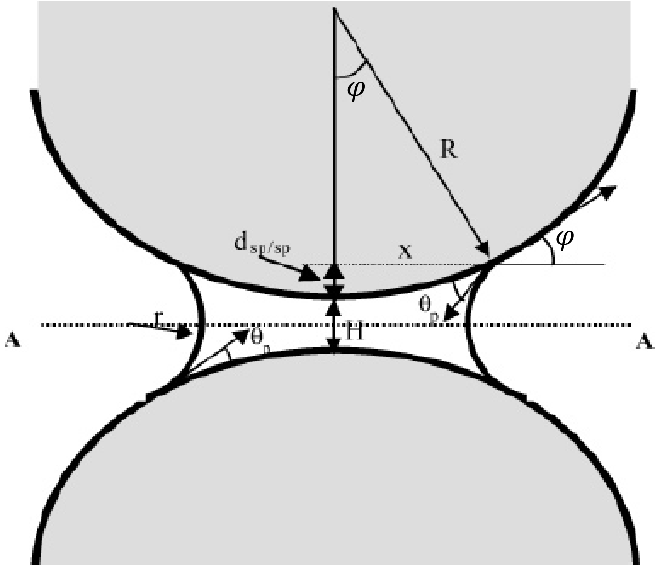
$$F_{cap,pp} = -\frac{4\pi R\gamma\cos\theta}{1+\left(\sqrt{1+\frac{2V_b}{\pi R h^2}}-1\right)^{-1}}$$

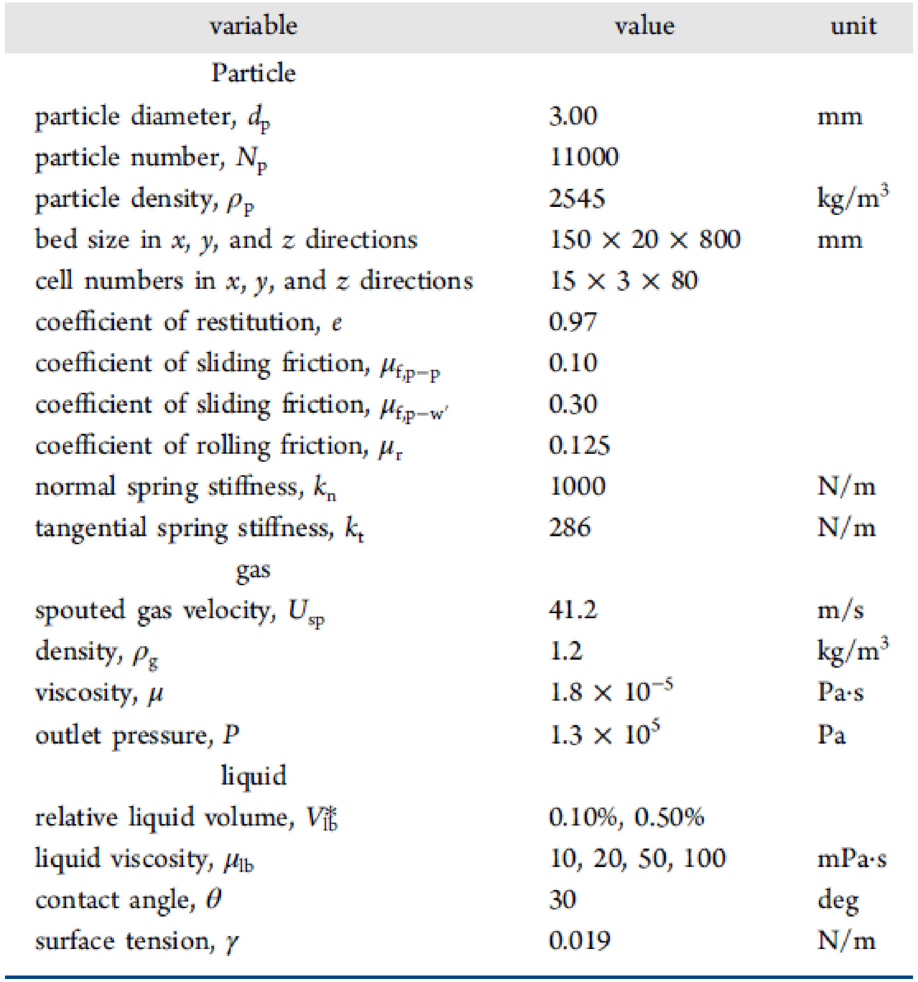




Spouted Bed Experiment/Model of Tang et al.







variable	value	unit
Particle		
particle diameter, d_p	3.00	mm
particle number, N_p	11000	
particle density, ρ_p	2545	kg/m^3
bed size in x, y, and z directions	150 × 20 × 800	mm
cell numbers in x, y, and z directions	15 × 3 × 80	
coefficient of restitution, e	0.97	
coefficient of sliding friction, $\mu_{f,p-p}$	0.10	
coefficient of sliding friction, $\mu_{f,p-w'}$	0.30	
coefficient of rolling friction, μ_r	0.125	
normal spring stiffness, k_n	1000	N/m
tangential spring stiffness, k_t	286	N/m
gas		
spouted gas velocity, U_{sp}	41.2	m/s
density, ρ_g	1.2	kg/m^3
viscosity, μ	1.8×10^{-5}	Pa·s
outlet pressure, P	1.3×10^5	Pa
liquid		
relative liquid volume, V_{lb}^*	0.10%, 0.50%	
liquid viscosity, μ_{lb}	10, 20, 50, 100	mPa·s
contact angle, θ	30	deg
surface tension, γ	0.019	N/m

- Tang et al.[3] modeled their experiment using MFiX-DEM; simulations were run for 15 s and results averaged over final 10 s
- Drag model used is Beetstra[4]
- Capillary force

$$F_{cp,n} = -\frac{2\pi\gamma R\cos\theta}{H/2d+1} - 2\pi\gamma R\sin\varphi\sin(\varphi+\theta)$$

- Viscous forces

$$\vec{F}_{v,n} = 6\pi\mu_{liq}R\frac{R}{H}\vec{v}_{rel,n}$$

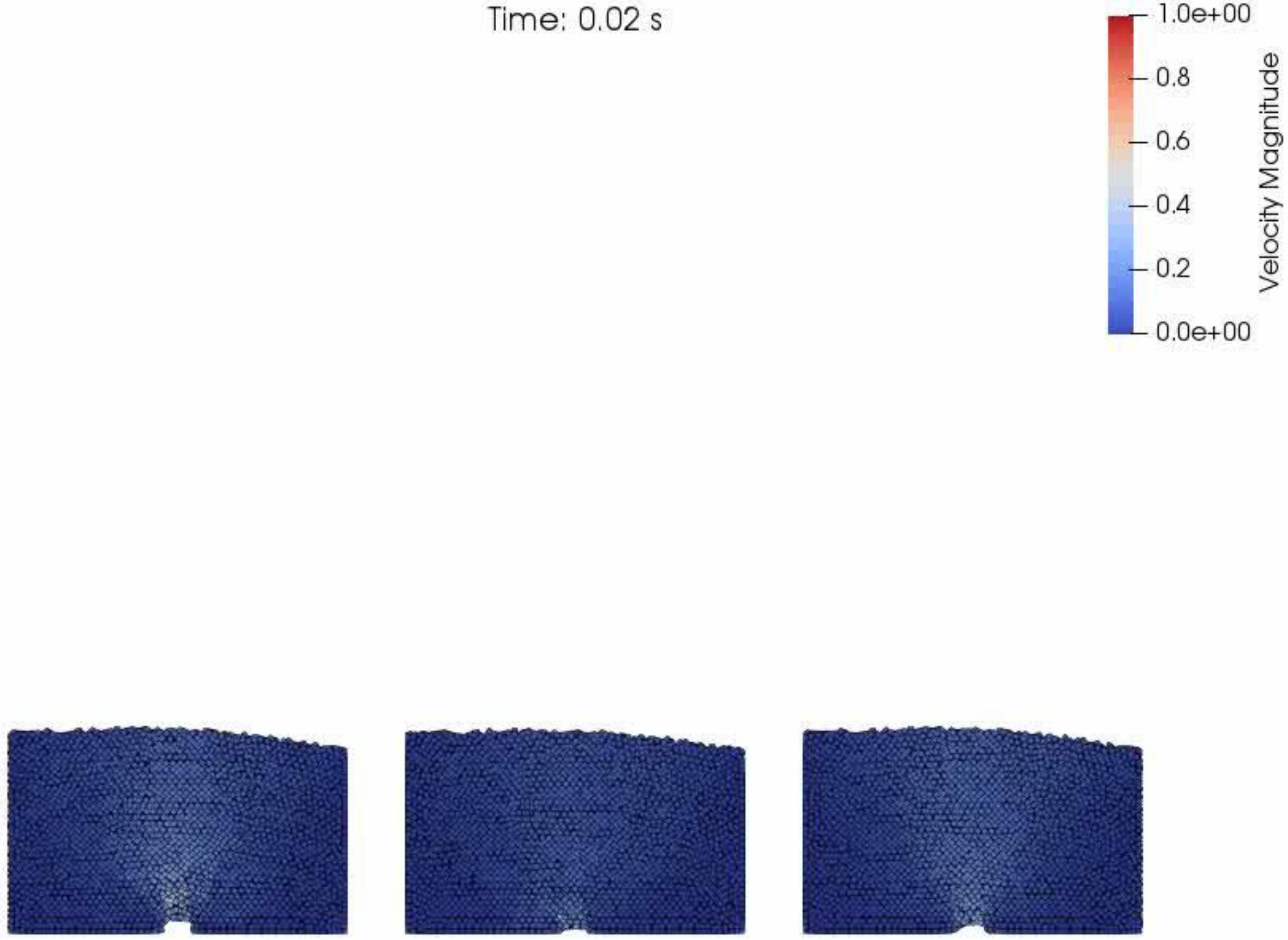
$$\vec{F}_{v,t} = 6\pi\mu_{liq}R(\frac{8}{15}\ln\frac{R}{H} + 0.9588)\vec{v}_{rel,t}$$

- Critical rupture distance

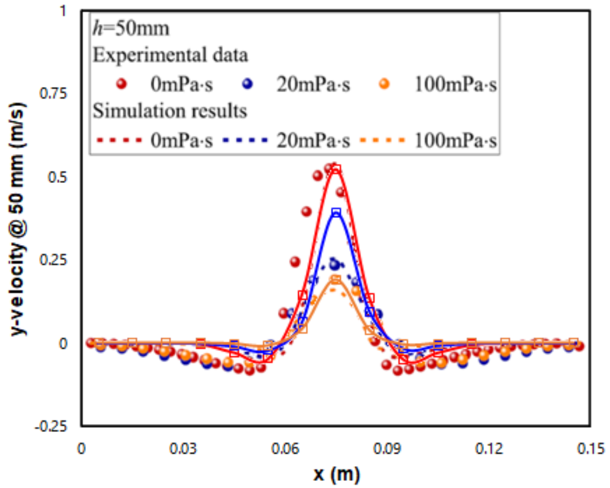
$$H_{cr} = R(0.5\theta+1)\sqrt[3]{\frac{V_{liq}}{R^3}}$$

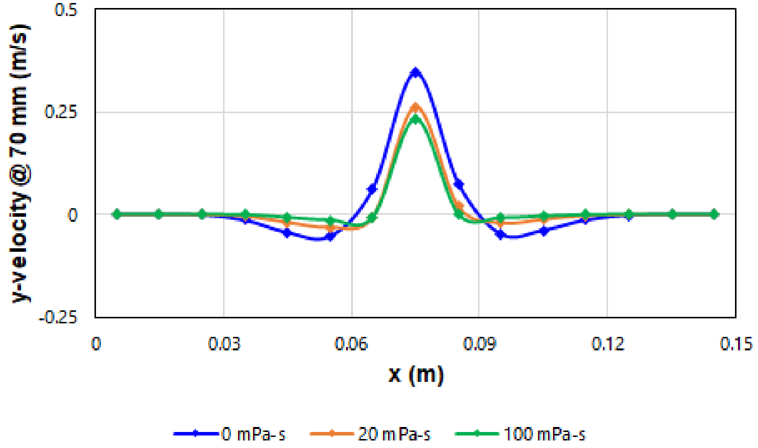
Wet Model Validation

Liquid Volume Fraction = 0.10%; Equivalent Film Radius = 0.5 μm



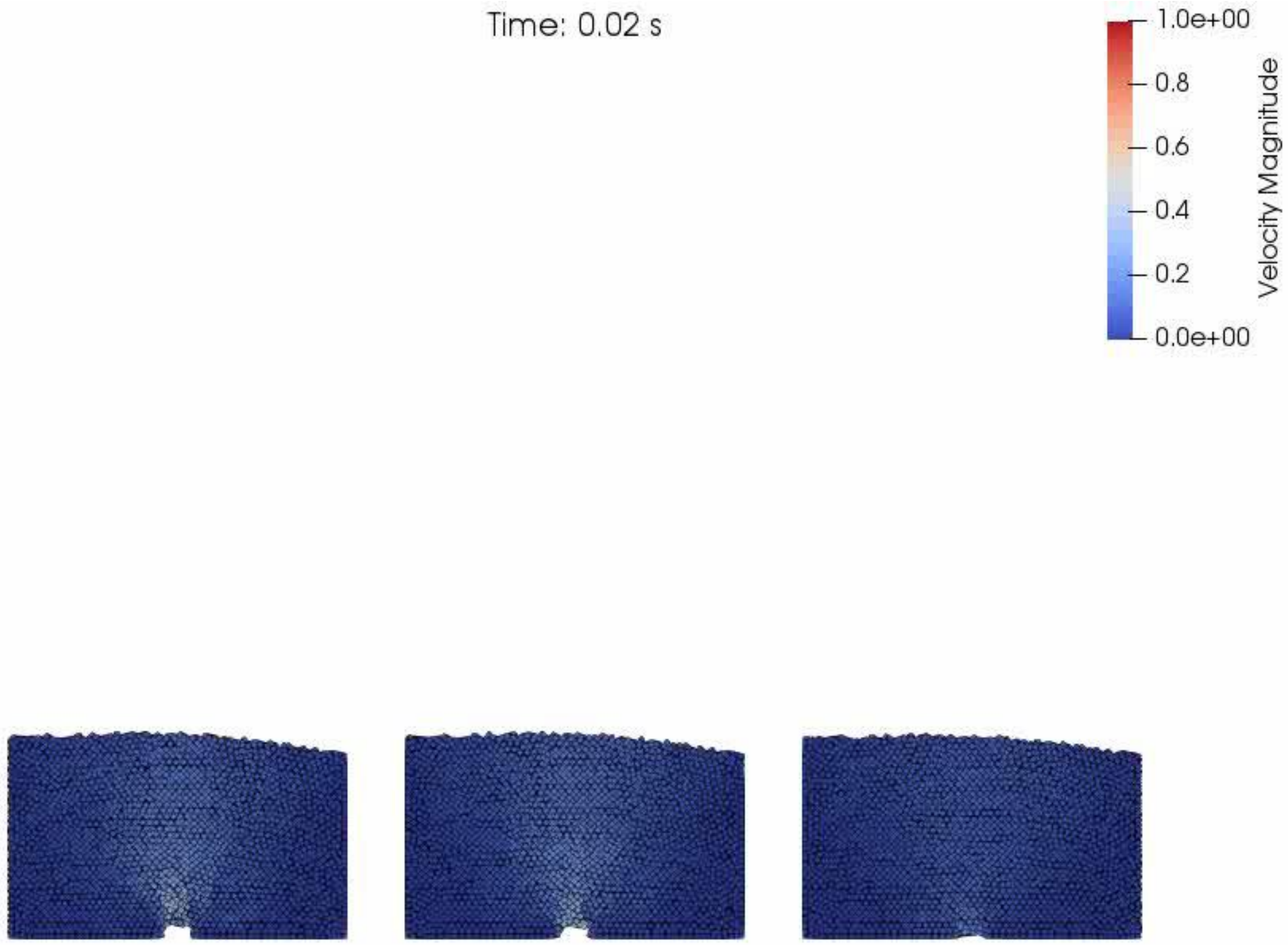
0 mPa-s 20 mPa-s 100 mPa-s





Effect of Liquid Volume

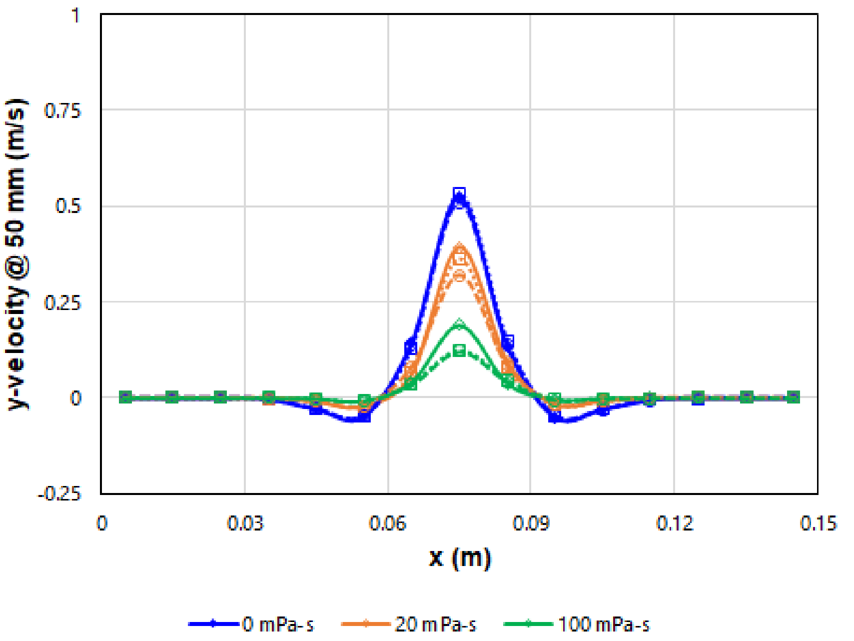
Liquid Volume Fraction = 10%



0 mPa-s

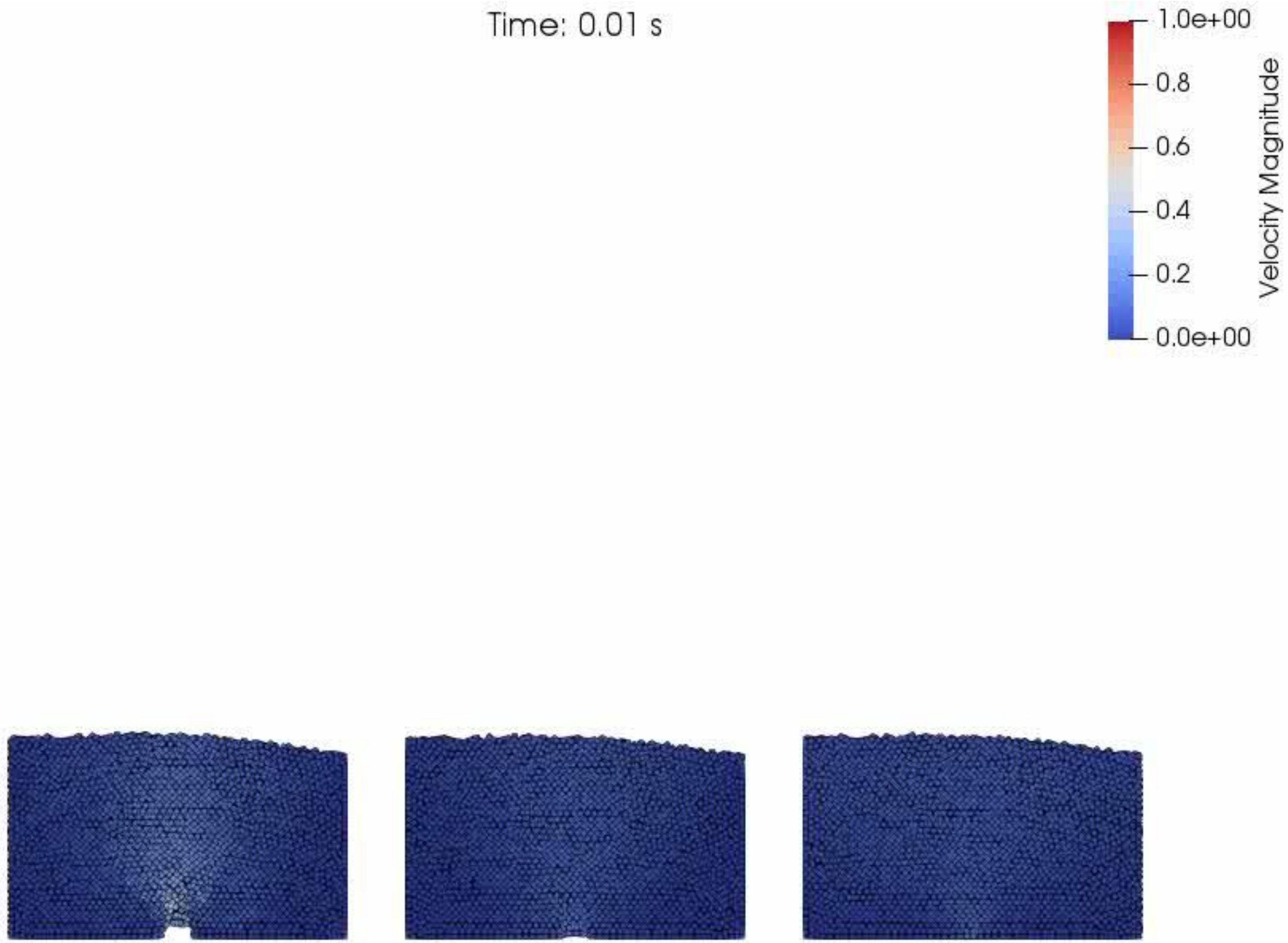
20 mPa-s

100 mPa-s



Effect of Liquid Viscosity

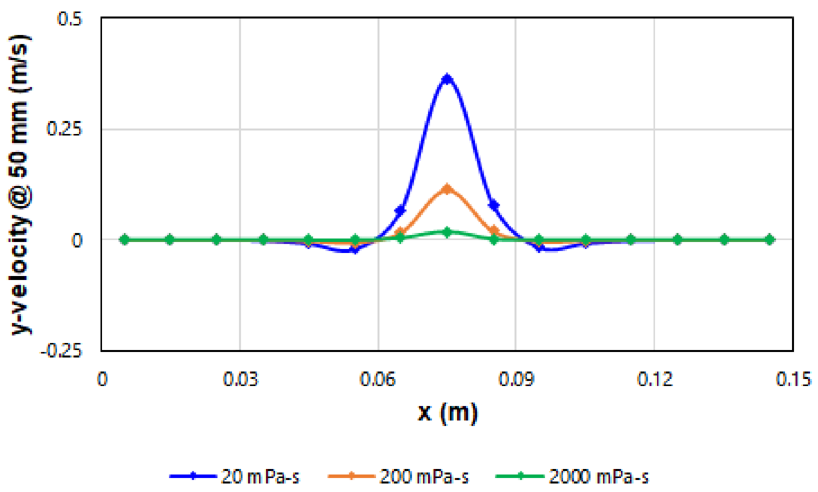
Liquid Volume Fraction = 50%

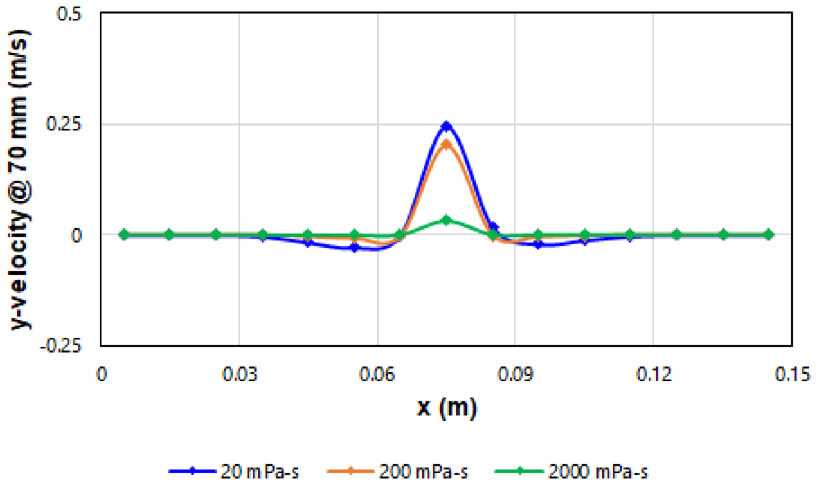


20 mPa-s

200 mPa-s

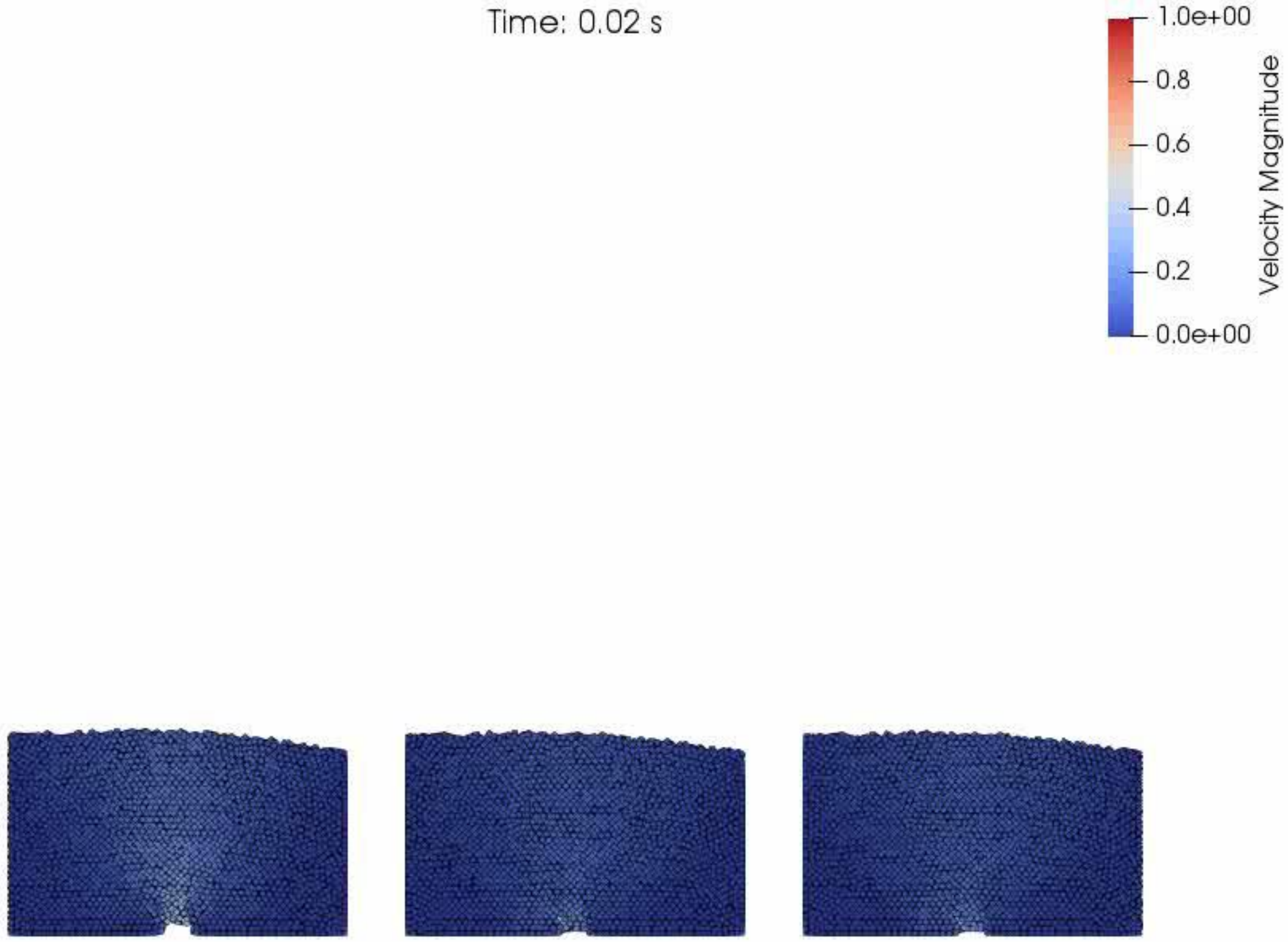
2000 mPa-s
(dtsolid reduced)



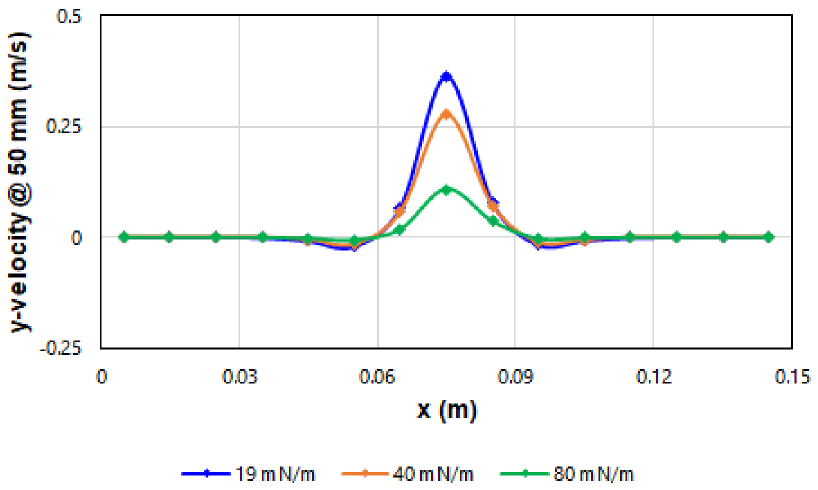


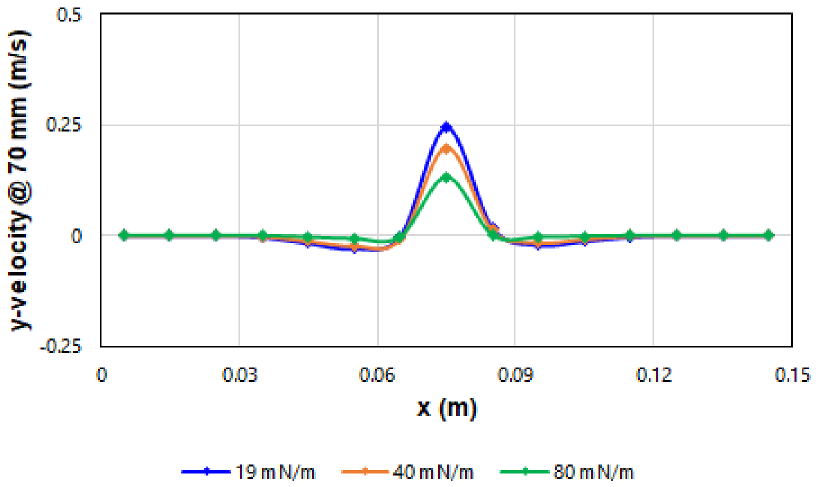
Effect of Liquid Surface Tension

Liquid Volume Fraction = 50%



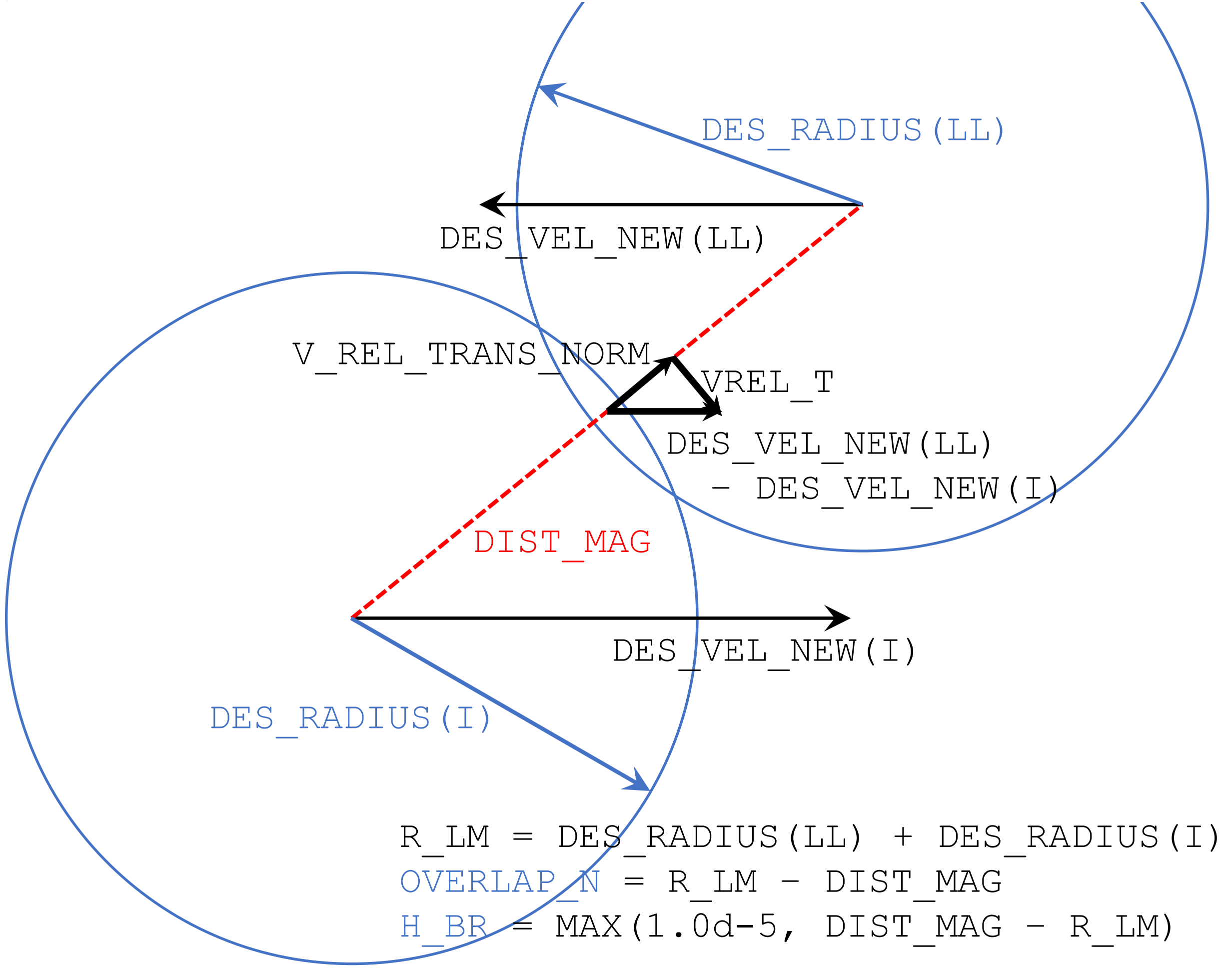
19 mN/m 40 mN/m 80 mN/m





Liquid Bridge Model Implementation for Pyrolysis

$$\vec{F}_{LB} = \left(\frac{2\pi R\gamma\cos\theta}{1+\left(\sqrt{1+2V/(\pi R H^2)}-1\right)^{-1}} - 6\pi\mu_{liq}R\frac{R}{H}\left|\vec{v}_{rel,n}\right| \right)\hat{n} - 6\pi\mu_{liq}R\left(\frac{8}{15}\ln\frac{R}{H}+0.9588\right)\vec{v}_{rel,t}$$



```
R_LM = DES_RADIUS(LL) + DES_RADIUS(I)
OVERLAP_N = R_LM - DIST_MAG
H_BR = MAX(1.0d-5, DIST_MAG - R_LM)
```

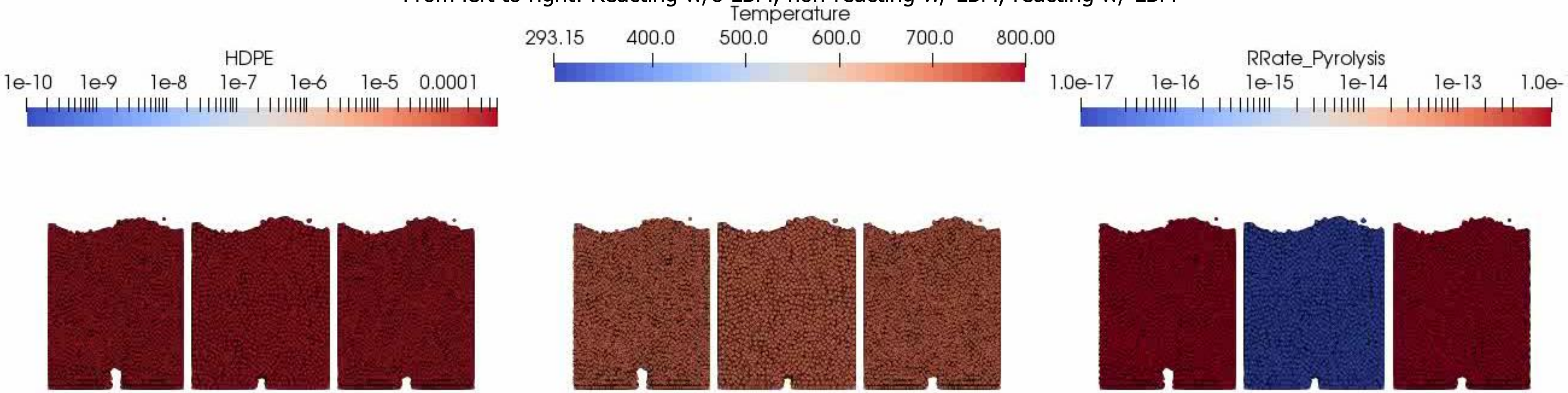
- The liquid bridge model in MFiX for cold flow was extended to implement a novel capability that explicitly models the mass, volume, and species of the liquid layer
- The evolution of the liquid bridge forces can be accurately modeled as the liquid volume changes (e.g., during pyrolysis)
- The “last species” volume is used to compute the capillary force instead of externally defined volume

```
volLL = DES_X_s(LL,NMAX(phaseLL)) * PMASS(LL)
  / RO_Xs0(phaseLL,NMAX(phaseLL))
```

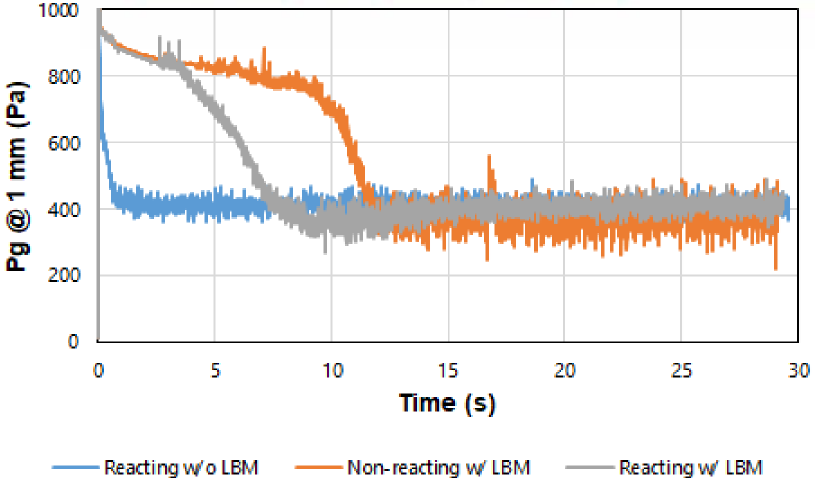
Transient Evolution of Liquid Layer Validation

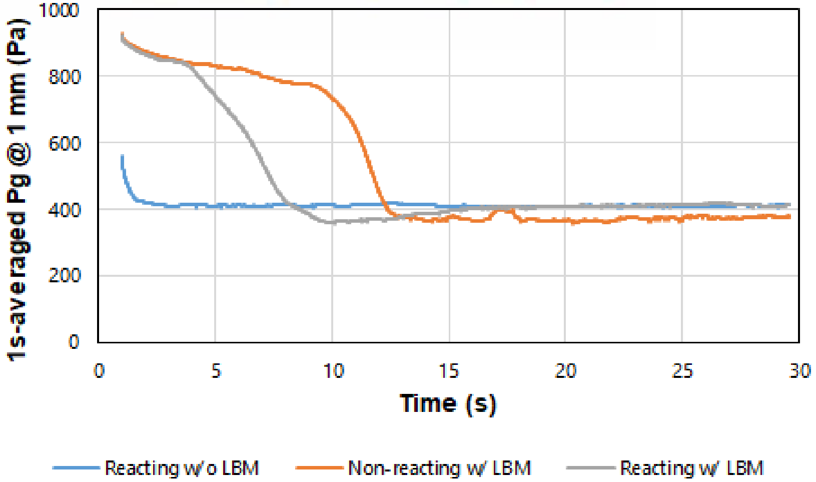
- Liquid layer in Tang et al.'s model is replaced with melted LDPE and allowed to pyrolyze to a gas pseudospecies: $\text{LDPE}_{(\text{liq})} \rightarrow \text{Volatiles}_{(\text{gas})}$, $A = 121.0 \cdot 10^9\ 1/s$, $E = 159 \cdot 10^3$ J/mol

From left to right: Reacting w/o LBM, non-reacting w/ LBM, reacting w/ LBM



Time: 0.05 s

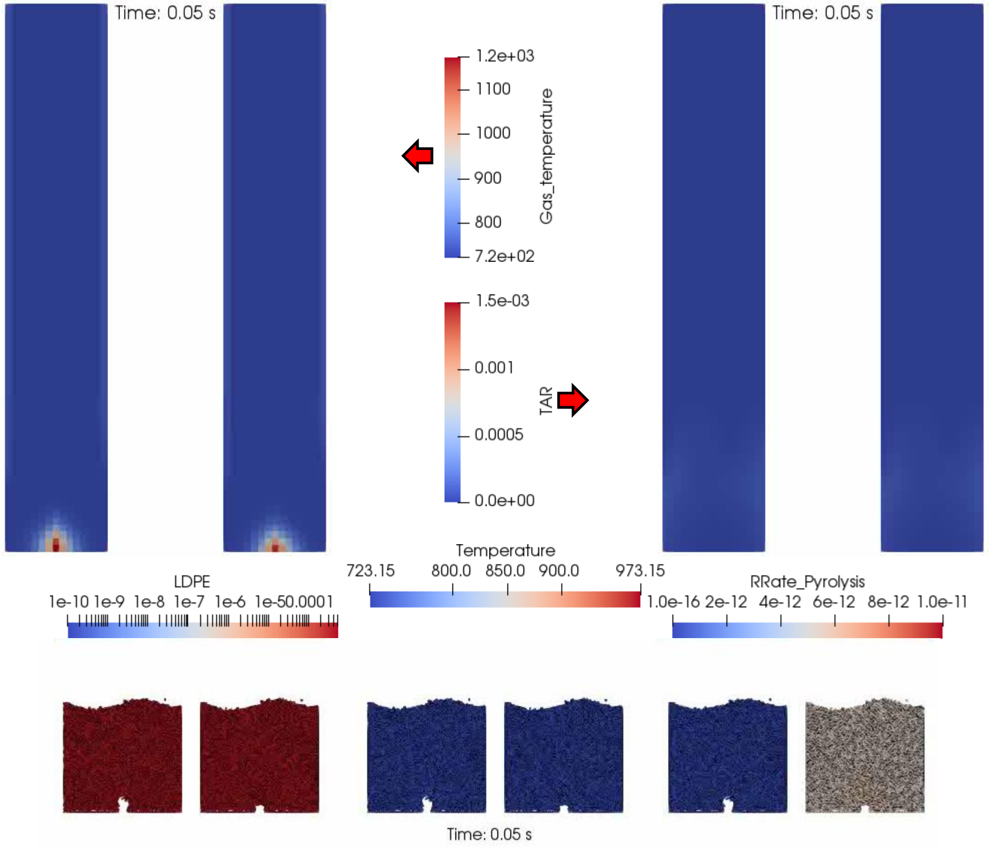


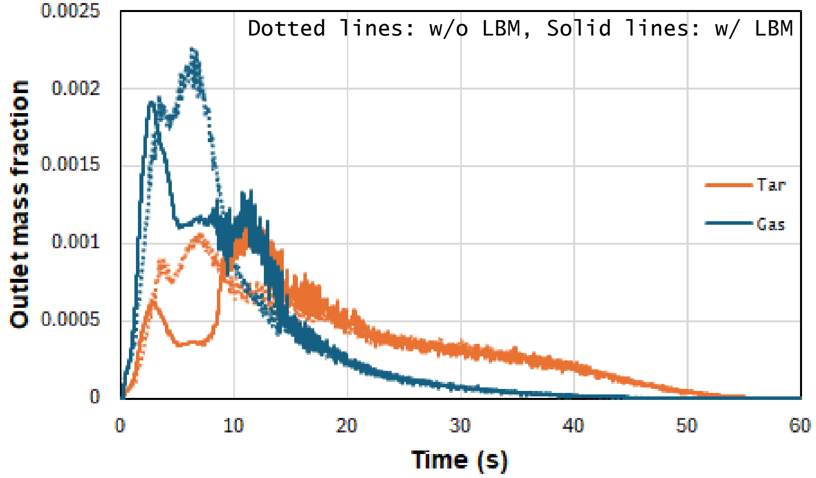


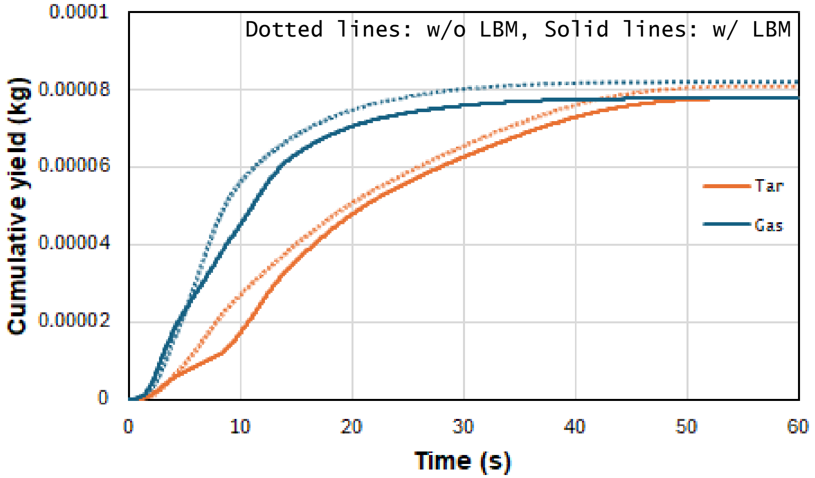
Effect of Agglomeration on Pyrolysis

- Reaction mechanism from Ding et al.[5]/Encinar et al.[6] simplifies pyrolysis products to separate pseudo-species representing gas and oils: LDPE → $0.4 \cdot \text{Gas} + 0.6 \cdot \text{Tar}$; $A = 2.30 \cdot 10^{18}\ \mathrm{s}^{-1}$; $E = 285.7\ \mathrm{MJ/kmol}$; $\Delta h = 975\ \mathrm{kJ/kg}$
- Tar → Gas; $A = 4.25 \cdot 10^{6}\ \mathrm{s}^{-1}$; $E = 108.0\ \mathrm{MJ/kmol}$; $\Delta h = -42\ \mathrm{kJ/kg}$

From left to right: Reacting w/o LBM, reacting w/ LBM

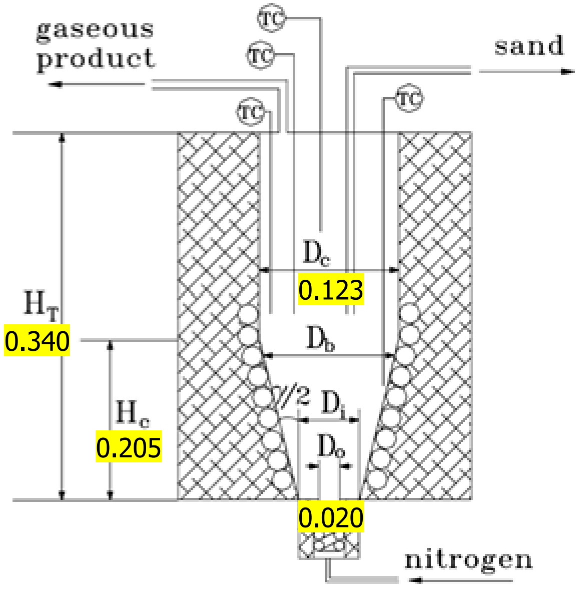






Continuous Operation Validation

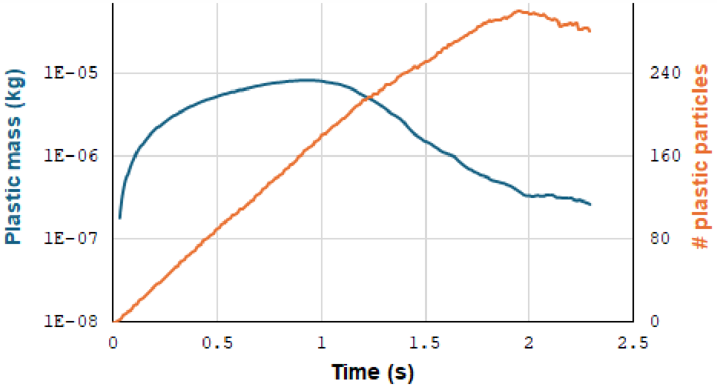
- Established CFD model of conical spouted bed reactor with continuous plastic feed based (loosely) on pilot-scale reactor of Aguado et al.[7]
  - As the plastic material is introduced into the reactor, it melts onto the sand particles and coats them
  - If the thickness of the layer that coats the particles is lower than a critical value, the sand particles do not fuse
  - Beyond this value, agglomerates grow irreversibly, and total blockage of the bed or defluidization is the result
- Good performance is determined on the basis of the critical thickness of the melted plastic that can be handled
- Sensitivity to solids holdup, material size/type, and fluidizing velocity can be compared

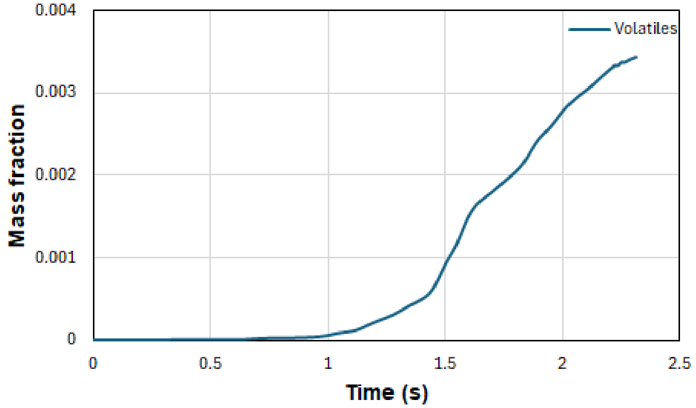


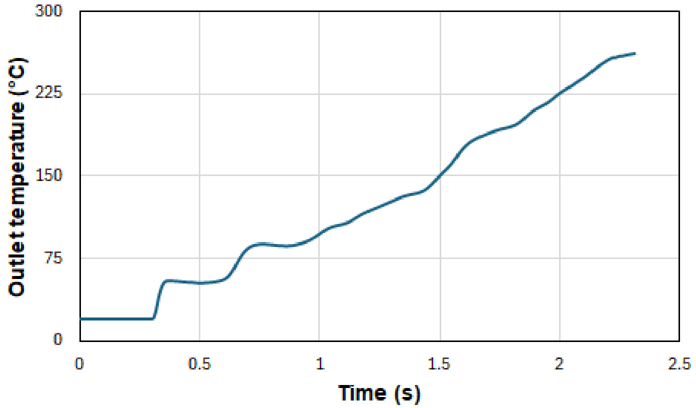
Variable	Value	Unit
bed size in x, y, and z directions	125 × 340 × 125	mm
cell numbers in x, y, and z directions	12 × 35 × 12	
Sand		
particle diameter, d_{p1}	1.00	mm
particle number, N_{p1}	22,000	
particle density, ρ_{p1}	2,600	kg/m³
Plastic (LDPE)		
particle diameter, d_{p2}	0.50	mm
particle density, ρ_{p2}	930.0	kg/m³
feed velocity, u_{p2}	0.0625	m/s
spouted gas velocity, U_{sp}	3.0	m/s
liquid viscosity, μ_{lb}	100.0	mPa·s

Baseline Results with No Melting

- Pyrolysis reaction occurs directly from plastic particles (no mass transfer to sand bed)

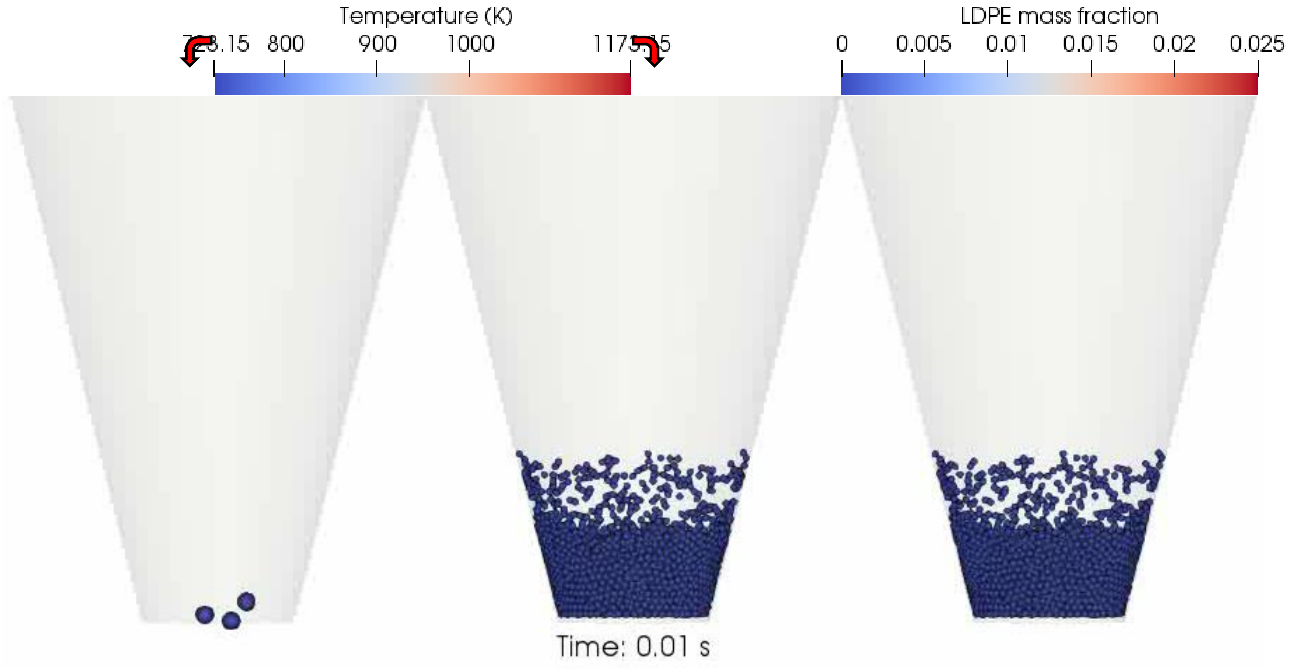


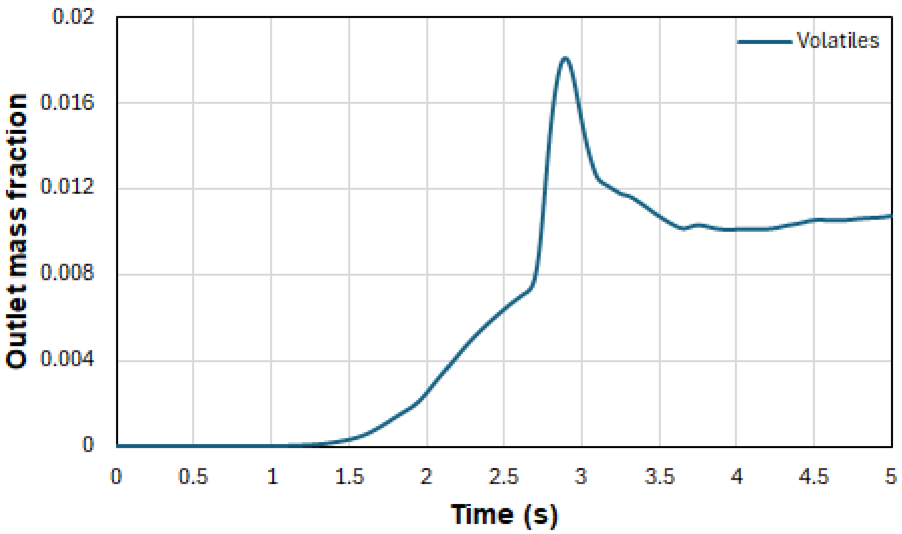




Results with Melting and Agglomeration

- Plastic particles ≳200 °C are considered to be melted and allowed to fuse with the sand particles on contact; the liquid volume is subsequently redistributed between sand particles during sand-sand collisions

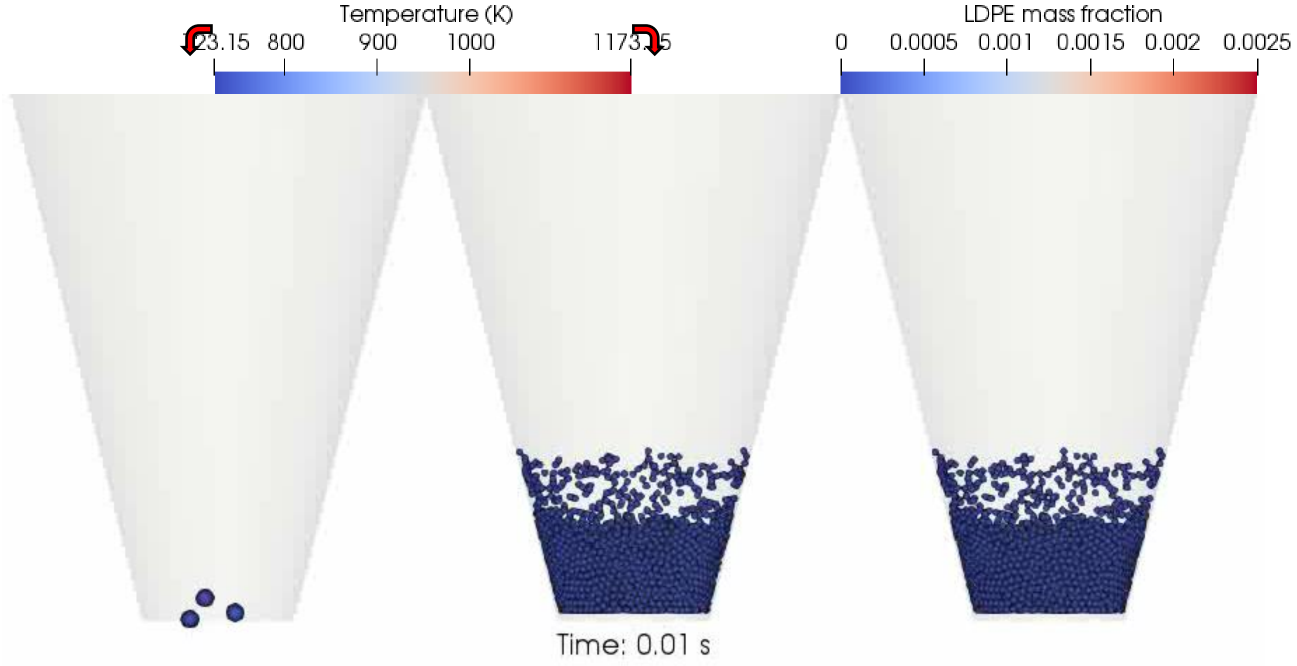


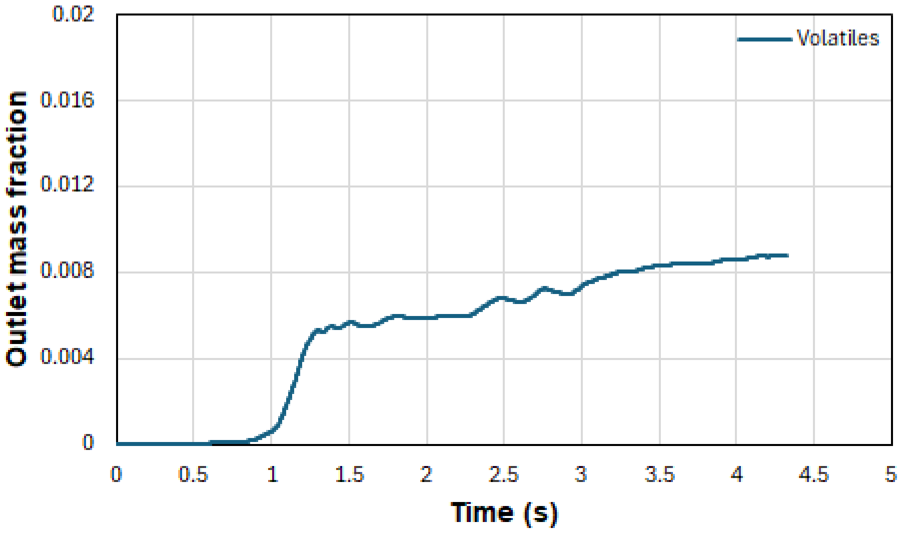


- Agglomeration due to cohesive liquid bridge forces causes the reactor to defluidize; the blockage dissipates when inlet velocity is increased from 3 m/s to 3.25 m/s after 2.5 s

Results with Melting and Agglomeration

- The agglomeration-induced defluidization occurs during initial startup when particle temperatures and hence pyrolysis rates are low
- If the startup velocity is 3.25 m/s for 2.5 s and subsequently reduced to 3 m/s, the bed is hot enough such that continuous operation prevails even at the lower velocity





- As such, the MFiX model with liquid bridge implementation can help to optimize the operating envelop for minimal impact on the performance of the pyrolysis reactor

Non-Instantaneous Liquid Distribution

- Dr. Tafti simulated the actual collision/coating process between liquid plastic and sand for a range of important non-dimensional ratios of inertial, viscous, and capillary forces
- For liquid viscosity of 1 kg/m-s (1000 mPa-s), the liquid transfer time was around 1 ms
- To incorporate a finite (i.e., non-instantaneous) liquid transfer time during the redistribution of the liquid layer during particle separation, the amount of mass transferred is multiplied by a coefficient

```
xferMass = 1.0d0 * abs(massLL - massI) / 2.d0
```

- The coefficient could be determined as a ratio of the collision time to the liquid transfer time constant from Dr. Tafti

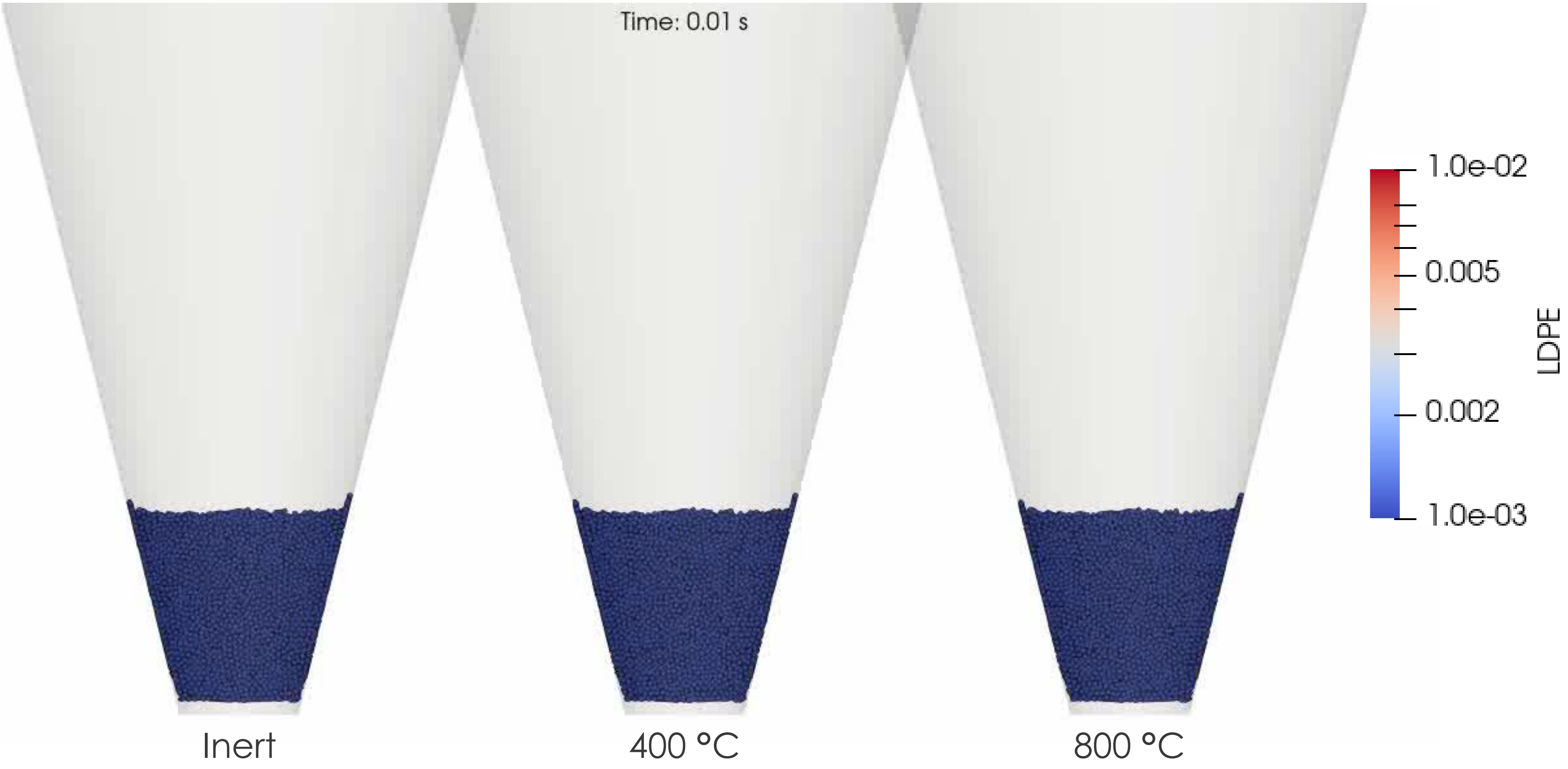
Non-Instantaneous Liquid Distribution

- Sensitivity to the mass transfer coefficient is determined for values of 1.0, 0.01, and 0.0001 (without reactions)

- The liquid transfer time is expected to be higher for more viscous plastics

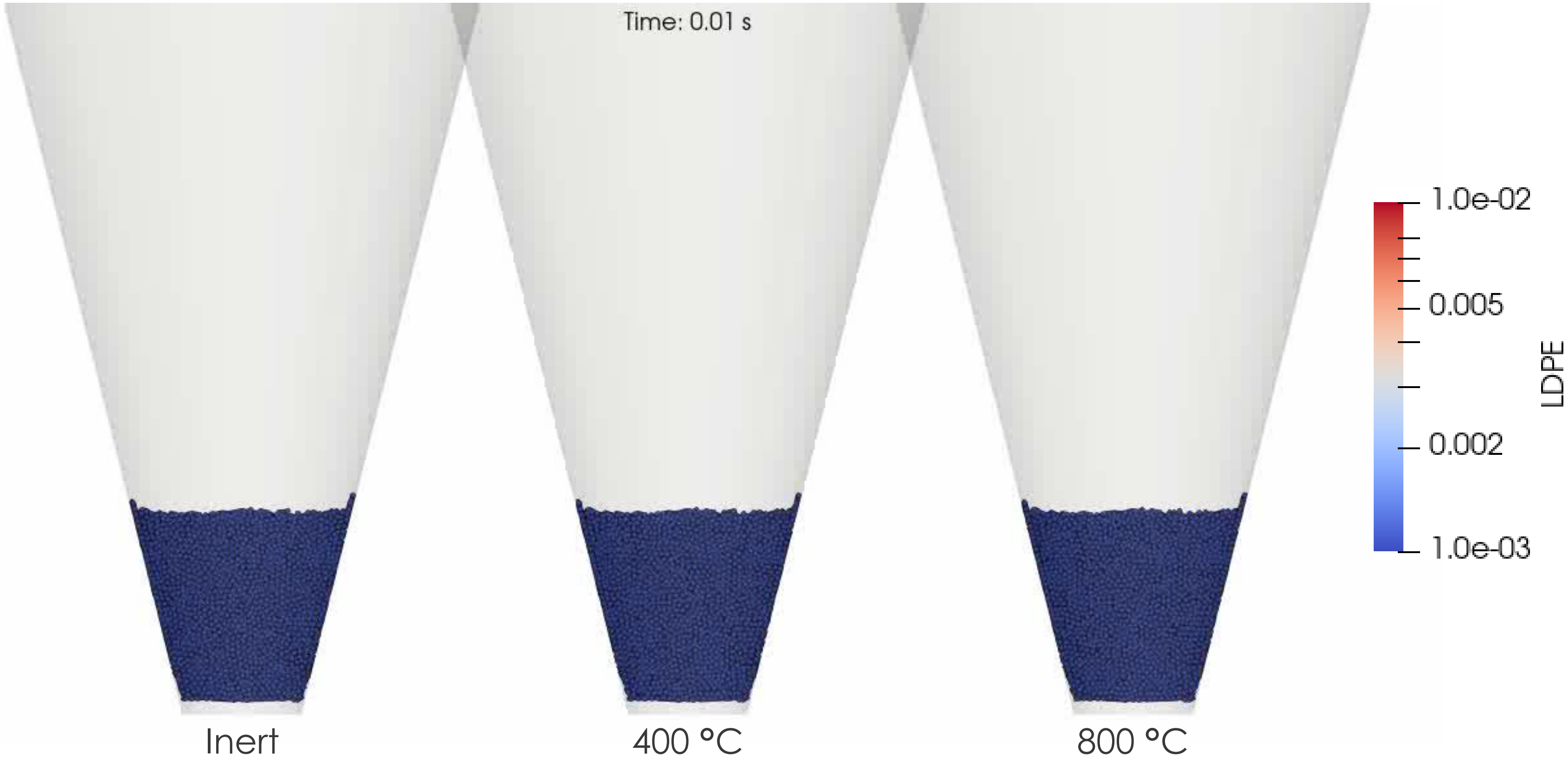
Instantaneous Liquid Distribution + Pyrolysis

- Repeat of earlier result with increased solids holdup and fixed mesh at different inlet temperatures compared with inert case
- Recall simplified reaction: $\mathrm{LDPE}_{(\mathrm{liq})} \rightarrow \mathrm{Volatiles}_{(\mathrm{gas})}$, $A = 121.0 \cdot 10^{9}$ 1/s , $E = 159 \cdot 10^{3}$ J/mol



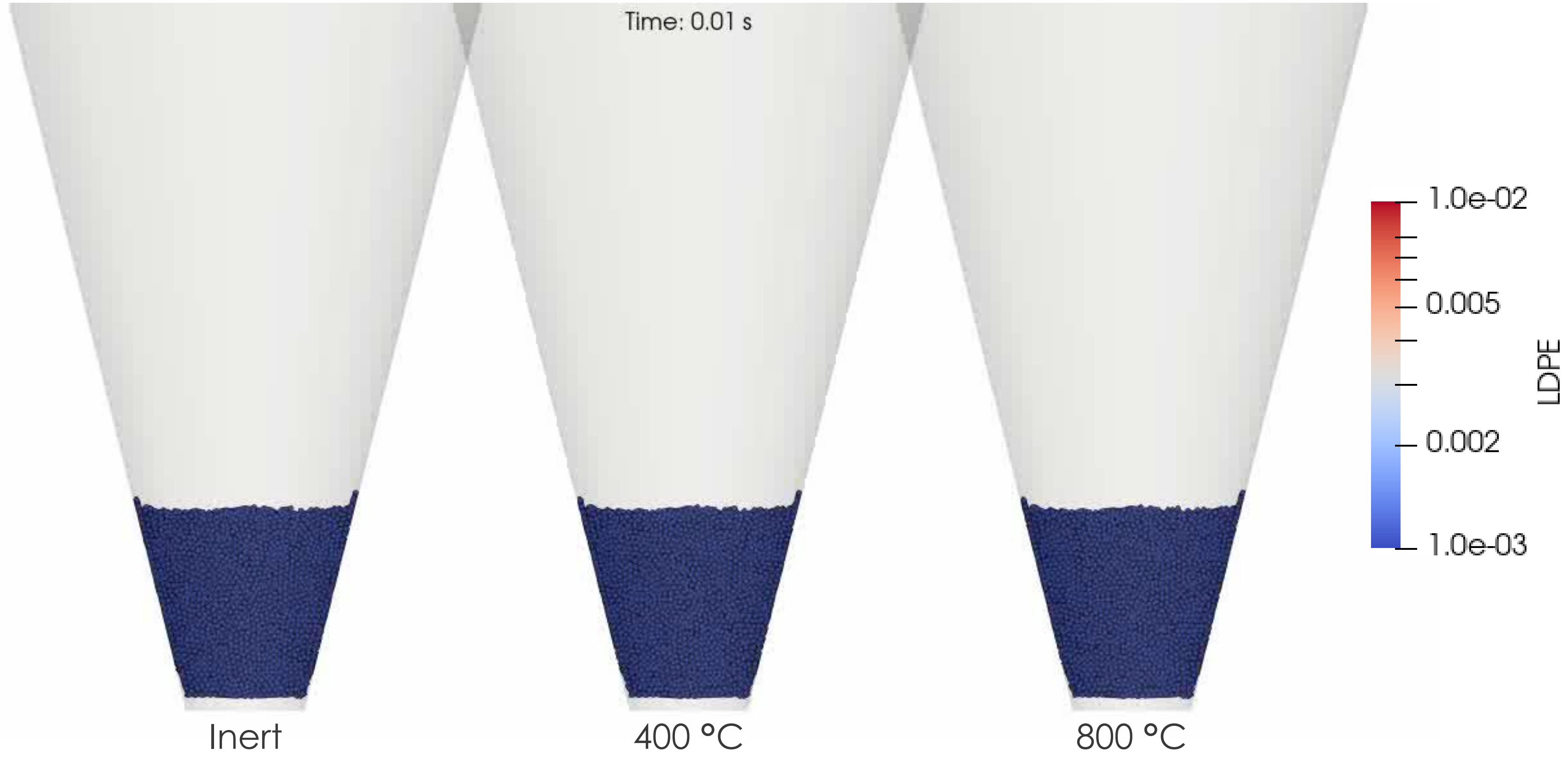
Non-Instantaneous Liquid Distribution + Pyrolysis

- Mass transfer ratio = 0.01



Non-Instantaneous Liquid Distribution + Pyrolysis

- Mass transfer ratio = 0.0001



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