A PYROPROBE DESIGN FOR MILLISECOND TIME-SCALE RESOLUTION FOR BIO-BASED SUSTAINABLE REACTION PRODUCTS

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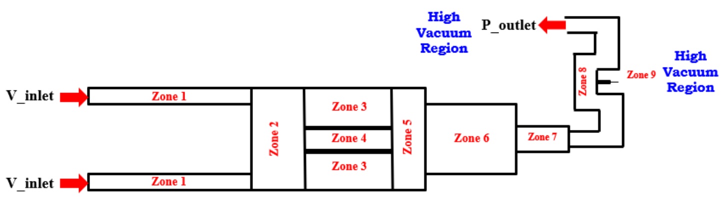
ABSTRACT: Existing commercial pyrolysis systems do not have the capability to perform millisecond-scale temporal analysis of the pyrolysis vapors. This capability would provide time-resolved experimental data on the various gas-phase intermediates predicted by density functional theory (DFT) models. To provide this capability, a novel experimental setup was designed by interfacing the probe rod from a CDS Analytical 5200 Series Pyroprobe system with a fast pulsing valve that can introduce micro-mole scale pulses of pyrolysis vapor into a synchrotron-based vacuum ultraviolet photoionization mass spectroscopy (SVUV-PIMS) instrument. CFD simulations for this modified pyroprobe system were performed using COMSOL Multiphysics®, which showed the average vapor residence time (τ) inside the probe to be about 180 ms for 280 ml/min inlet flow. This millisecond range residence time of the modified pyroprobe is well-suited to interrogate the primary fast pyrolysis reactions by mapping the time evolution profiles of the nascent reactive/stable intermediates.

Simplified Geometry & Location of Zones



Zone	Location	Flow Regime
Zone 1	Annulus Region	Continuum ($Kn \leq 10^{-3}$)
Zone 2	Between probe rod and quartz tube	
Zone 3	Between interface and quartz tube	
Zone 4	Quartz tube	
Zone 5	Between interface outlet and quartz tube	
Zone 6	Interface stem	
Zone 7	Internal bore in the union fitting	
Zone 8	Pulse valve base	
Zone 9	Internal bore & 0.004" Orifice	Free Molecular ($Kn \geq 10$)

Governing Equations, Assumptions & Boundary Conditions

Equation of motion for a Newtonian fluid (Zones 1-8): $\rho \frac{Dv}{Dt} = -\nabla p + \mu \nabla^2 v + \rho g$

Equation of change (Zone 9): $\frac{\delta c_i}{\delta t} - D\frac{\delta^2 c_i}{\delta x^2} = R_i$

$$D = \frac{2}{3P\sigma_A^2}\sqrt{\frac{K_B^3 N_A T^3}{\pi^3 M_A}}$$ (Self-Diffusion Coefficient, *c.a.* 4.37×10^2 m²/s)

Assumptions

- Steady-state (Zones 1-8)
- Isothermal (T = 298 K)
- Flow is uniformly distributed at the inlet

Boundary Conditions for Zones 1 to 8

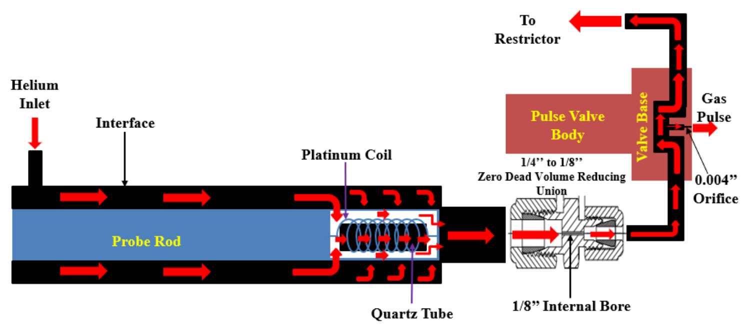
- Inlet V = 0.25261 m²/s or Q = 280 ml/min
- Equal velocity at the interface between zones
- Outlet P = 50 to 760 Torr

Boundary Conditions for Zone 9

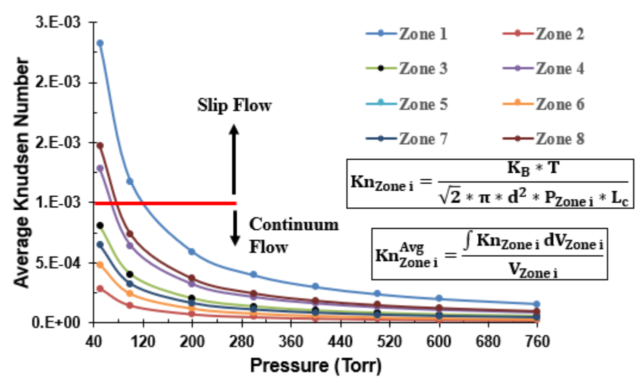
- Inlet $F_0 = \left(\frac{N_0}{N_A * A_{bore}}\right)\left(\frac{t}{\tau^2}\right)e^{\left(-\frac{t}{\tau}\right)}$
- Outlet $F_{out} = -\frac{V_p * c}{A_{orifice}}$

τ = 1 ms, t = 0 – 1 s, $N_0 = 10^{12}$ molecules, V_p = 200 l/s, $A_{bore} = 4.87 \times 10^{-7}$ m² & $A_{orifice} = 8.11 \times 10^{-9}$ m²

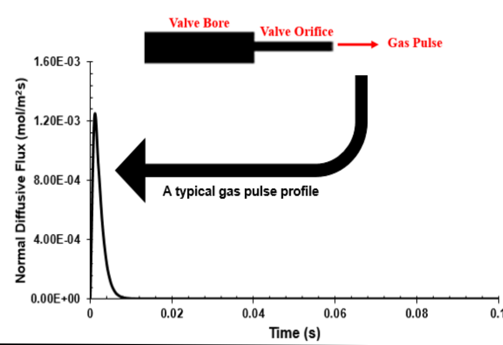
Schematic of the Modified Pyroprobe Reactor



Key Results



Simulated Gas Pulse Intensity Profile for a 1ms Pulse Width



Conclusions

- **Slip flow regime** is observed in Zone 1 when P_{out} = 50 and 120 Torr.
- **Slip flow regime** is observed in Zones 4 & 8 when P_{out} < 100 Torr.
- Flow remains in **continuum regime** in zones 3 & 5-7 for all P_{out} values.
- The **ΔP** across the system is constant (*ca.* 0.14 Torr) for all outlet pressures to maintain a constant inlet flowrate (280 ml/min).
- Due to the constant ΔP, the average values of **U, Q & Re** in each zone across all the outlet pressures are also constant.
- The **residence time (τ)** for a molecule to reach the pulse valve orifice from the sample holder is *ca.* **180 ms**.

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