Methane Oxidation and Combustion Chemistry

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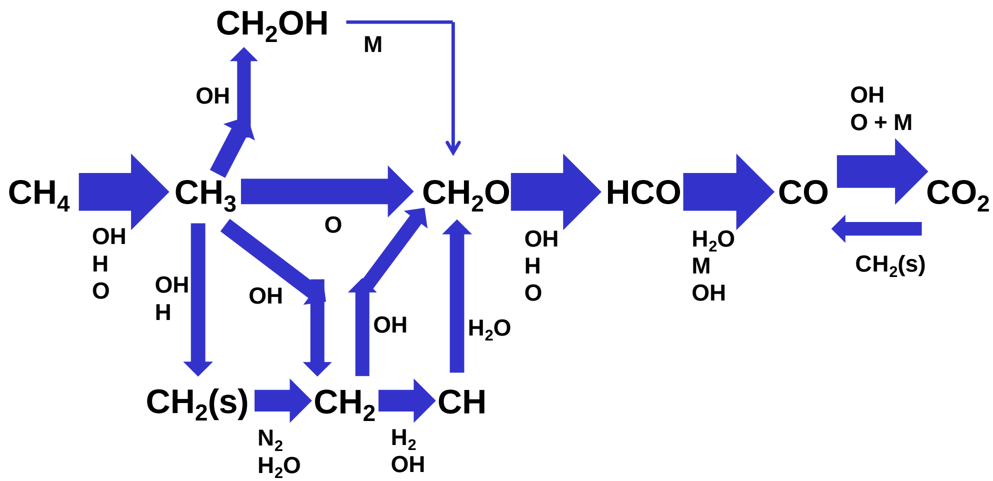
Introduction/Background

- Personal Background: **Eric Petersen**
  - 20 Years of experience in hydrocarbon combustion and related chemical kinetics measurements
  - Chaired Professor in Dept. of Mechanical Engineering at Texas A&M University
  - 36 journal and 100+ conference publications related to methane combustion and oxidation chemistry

- **Texas A&M University** and Turbomachinery Laboratory
  - Petersen Research Group: combustion experiments
  - Kulatilaka Group: optical diagnostics for reacting flows
  - Simon North (Chemistry): atmospheric chemistry

State of the Art on CH_4 Oxidation Kinetics



- Chemical Kinetics Models for Predicting CH_4 and NG Oxidation
  - **GRI 3.0**: mechanism from 2000 (53 species, 325 rxns)
  - **AramcoMech 3.0**, 2018 (Curran et al.): for NG up to C5 (581 spec, 3037 rxns)
  - Several others (USCMech; Glarborg; Princeton; etc.)

- Current Validation:
  - **T = 800 – 2500 K**
  - **P = 1 – 50 atm** (fairly well known); **50+ atm** (some validation)
  - Fuel-to-air equivalence ratio: **ϕ = 0.5 – 2.0** (5 – 17% CH_4)

Ignition Chemistry

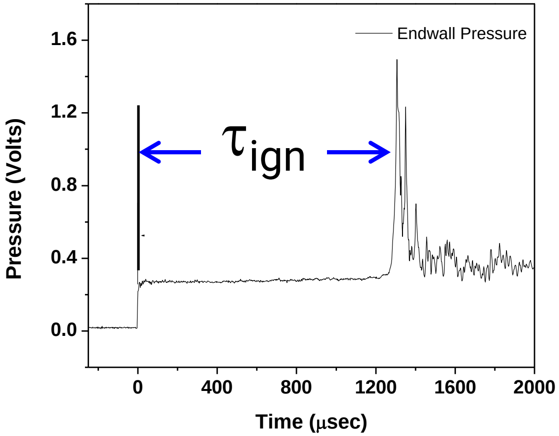
Ignition Delay Times Help Define Overall Kinetics Mechanism Reactivity

Ignition Delay Times for NG Blend

Lines = model

Experimental Methodology

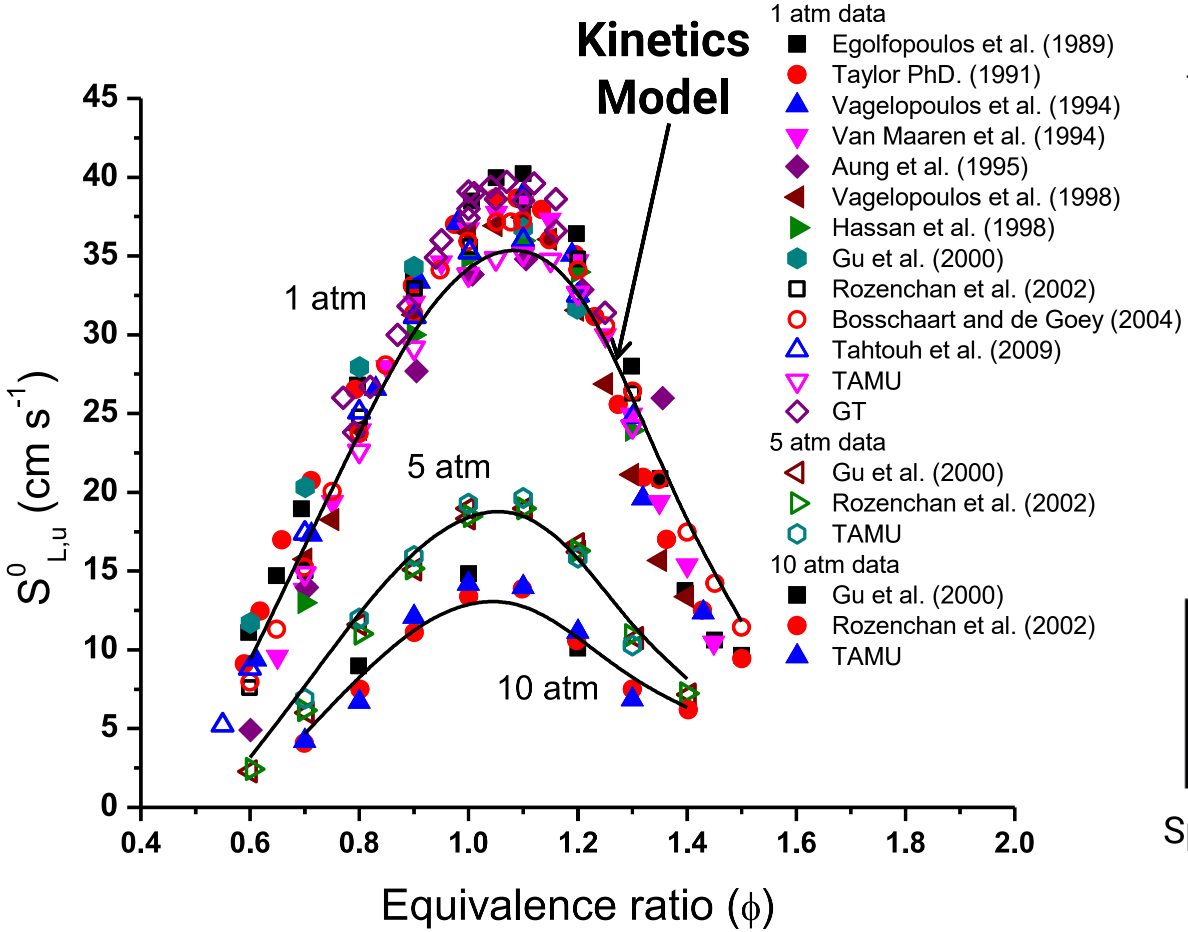
High Pressure Shock Tube at TAMU



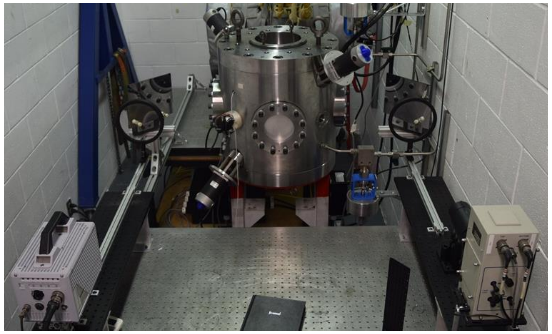
Ignition Delay Time Measurement

Laminar Flame Speed

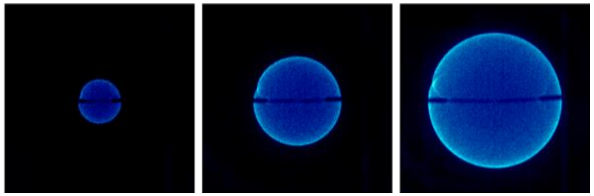
Methane Laminar Flame Speed is fairly well studied



Experimental Methodology



Constant-Volume Vessels at TAMU

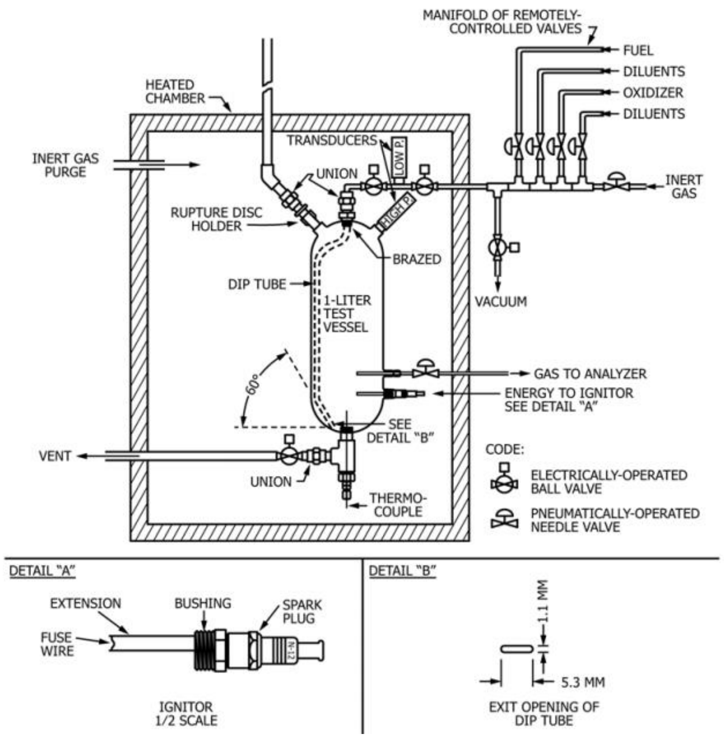


Spherical, Laminar Flame Propagation

Lean Flammability Limit

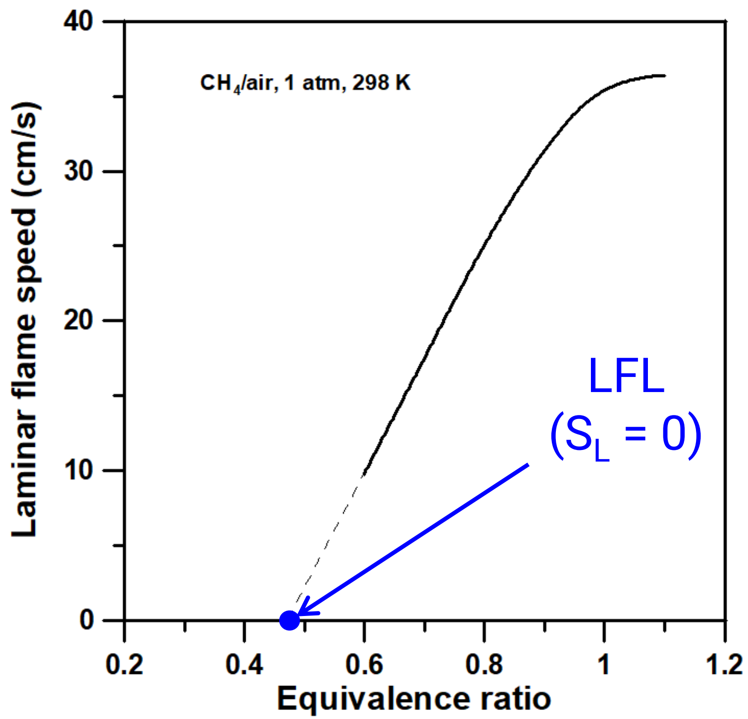
Flammability Limits are routinely measured, but kinetics models are now good enough to do some predictions of LFL

Experimental Methodology



FL Apparatus (from ASTM E918-19)

Calculated from Flame Speed Kinetics



Key Reaction Steps and Effect of Radicals

Reactivity of methane oxidation depends greatly on radicals (**OH**, **O**, **H**, HO_2, **CH_3**)

$CH_4 + \mathbf{H} \rightarrow \mathbf{CH_3} + H_2$

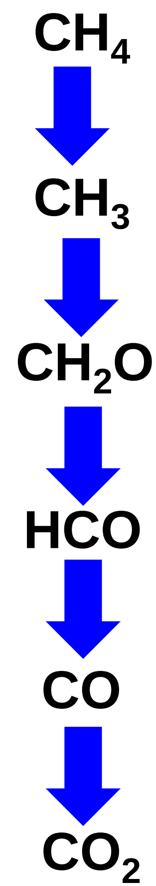
$CH_4 + \mathbf{OH} \rightarrow \mathbf{CH_3} + H_2O$

$CH_4 + \mathbf{O} \rightarrow \mathbf{CH_3} + \mathbf{OH}$

$\mathbf{CH_3} + O_2 \rightarrow CH_2O + \mathbf{OH}$

$\mathbf{H} + O_2 \rightarrow \mathbf{OH} + \mathbf{O}$

$CH_2O + \mathbf{OH} \rightarrow HCO + H_2O$



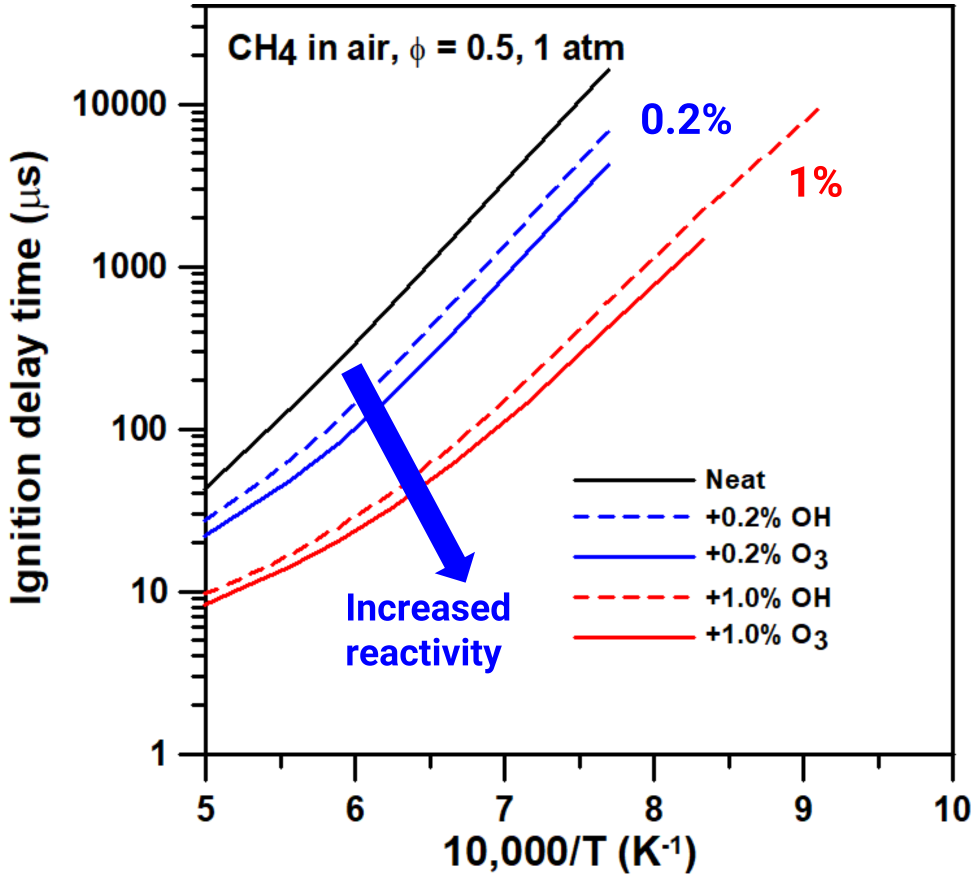
Effect of Additives and Impurities on CH_4 Combustion

Reactivity and ignition of CH_4 can be sped up using additives

- HC impurities already in Natural Gas
  - C_2H_6
  - C_3H_8
  - C_4H_{10}, C_5H_{12}
- Hydrogen (leads to H, OH radicals)
- Silane; others (basically anything that produces H atoms)
- NO_2, N_2O, **Ozone**? (basically anything leading to OH or O)

OH Radical and Ozone Seeding

Models can be used to estimate effect of OH and O_3 addition to CH_4-Air combustion process

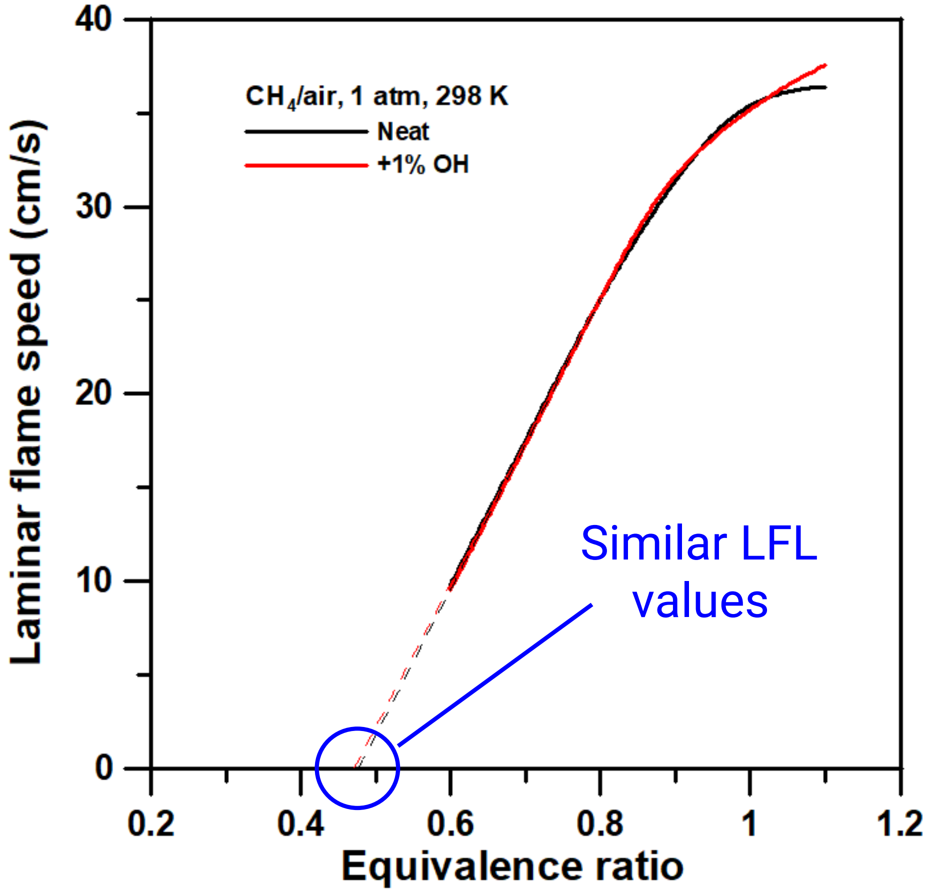


- Calcs using AramcoMech model
- CH_4 – Air at ϕ = 0.5
- OH represents infusion of radicals, for basic trend
- O_3 submechanism taken from Ju et al. (2016)

Effects of Seeding on CH_4 LFL

Models can be used to estimate effect of additives on to CH_4 LFL Using Laminar Flame Speed

- Preliminary calcs using AramcoMech model
- CH_4 – Air at 1 atm
- OH represents infusion of radicals, for basic trend
- No real effect, but verdict is out for other additives, TBD
- Can use method for other mixture and conditions



Current Knowledge Gaps on CH_4 Chemical Kinetics

- Deficiencies in our ability to predict CH_4 chemical kinetics for:
  - Very lean conditions, $\phi < 0.5$ ($CH_4 < 5\%$)
  - Effect of additives and impurities on flammability limits in general
  - Effect of additives and impurities on ignition at very lean conditions