Preignition Chemistry of Xylenes and Their Effect on JP-8 Surrogates

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Motivation

• Roubaud et al. (2000a) at CNRS investigated neat xylene autoignition in a rapid compression machine and found the reactivity in descending order: o-xylene (1,2-dimethylbenzene), m-xylene (1,3-dimethylbenzene), p-xylene (1,4-dimethylbenzene)

• Violi et al. (2002) at Utah developed a surrogate of 30% n-dodecane / 20% n-tetradecane / 20% methylcyclohexane / 15% m-xylene / 10% iso-octane / 5% tetralin by volume (S6) that matched the class composition and distillation properties of JP-8

• Seshadri (2006) at UCSD found that a modified Violi surrogate with o-xylene was less reactive in non-premixed counterflow flame experiments than with m-xylene and thus a better surrogate for JP-8

• Holley et al. (2007) at USC found that the Violi surrogate was more reactive than JP-8 in non-premixed counterflow flame experiments (as expected)

➔ In summary, conflicting results on the reactivity of the xylenes in surrogates
Background

• Emdee et al. (1990, 1991) at Princeton studied the neat xylenes in an atmospheric flow reactor at 1093-1199 K and $\phi = 0.47-1.7$
  – o-Xylene was the most reactive, followed by p-xylene and m-xylene
  – High temperature branching pathways via o-xylylene were identified

• Gail and Dagaut (2005, 2007) at CNRS studied neat p- and m-xylene in an atmospheric jet-stirred reactor at 900-1300 K and $\phi = 0.5-1.5$
  – p-Xylene was slightly more reactive than m-xylene

• Roubaud et al. (2000b) at CNRS studied neat o-xylene in a rapid compression machine at 600-900 K and stoichiometric equivalence ratio
  – Low temperature autoignition pathway of o-xylene was similar to Emdee et al. (1990)

→ At high temperatures, comprehensive work has been conducted comparing the neat xylene isomers

→ However, at low and intermediate temperatures, past neat xylene work is scarce
  → Difficult to initiate reactivity of neat xylene isomers at low and intermediate temperatures and lean equivalence ratios
Program Overview

- Objectives:
  1) Explore the preignition and autoignition reactivity differences of the xylenes
  2) Compare the relative reactivity of the xylene isomers in JP-8 surrogates
  3) Isolate the key branching pathways of xylene oxidation

- Approach:
  - Stress and/or react the fuel/oxidizer/diluent systems under well controlled conditions in our Pressurized Flow Reactor (PFR) and Single Cylinder Research Engine
    » Perform bench scale tests on the xylene isomers neat and in binary mixtures with paraffins
    » Monitor reactivity and collect gas samples as a function of experimental and reactant conditions
    » Perform detailed chemical analysis of extracted gas samples
  - Mechanistic analysis and development
  - JP-8 surrogate development
    » Vary the xylene isomer in proposed JP-8 surrogates and compare the oxidation reactivity in our facilities
PFR Facility

Temperature: 600 – 850 K
Pressure: 2 – 16 atm
Quartz Reactor ID: 2.2 cm
Quartz Reactor Length: 40 cm

Nitrogen
Oxygen
Nitrogen Diluent

3kW Heater
Fuel

10kW Heater
Mixing Nozzle
Quartz Reactor
Gas Sampling Probe & TC
Pressure Transducers

Pressure Regulating Valve
Exhaust

Exhaust

On-line Analyzers CO/CO₂/O₂ NDIR
Off-line Analyzers GC/MS & GC/FID

Sample Storage Cart
Computer Controlled Probe Positioning Table
Data Control & Acquisition System

Probe Cooling System
• CO is the major indicator of reactivity at low temperatures
• Measurements are ±50 ppm for CO and CO₂, and ±1250 ppm for O₂
GC/MS/FID Facility

- Samples from PFR collected in 10-ml loops in sample storage cart heated to 180°C
- Samples injected into GC/MS/FID for analysis
- Separation aided by sub-ambient initial oven temperature
- Identification performed by mass spectra compared to NIST MS Version 2.0
- Supelco Petrocol DH column in GC
  - 100 m, 0.5 μm film thickness
  - 0.25 mm OD, 1250 Phase Ratio (β)
- MS parameters
  - Ion source 200°C
  - Electron ionization -70eV
  - Multiplier voltage 1456 V
  - Emission current 100 μA

GC temperature ramp
Engine Parameters

- Speed: 750 RPM
- Bore: 8.25 cm
- Stroke: 11.43 cm
- Displacement: 611 cm$^3$
- Compression ratio: 16:1
- Equivalence ratio: 0.26
- Inlet pressure: 0.1 MPa
- Inlet temperature: 427 K

- IVO: 10° bTDC
- IVC: 34° aBDC (214 CAD)
- EVO: 40° bBDC
- EVC: 15° aTDC

- Measurements are ±0.2 CAD

- Conditions selected for JP-8 and n-dodecane testing

- Temperature rise (calculated) due to isentropic compression of air at engine conditions, time = 0 ms at IVC and time = 32.2 ms at TDC
  - Specific heats from Chase (1998)
  - $T_{\text{max}}, \Delta S=0, \text{Air} : 1054$ K

- 25 ms is ~330 CAD with $T\sim810$ K

![Diagram of temperature over time](image-url)
Comparison to Kinetic Models

- Ranzi et al. (2007) model from Politecnico di Milano
  - Semi-detailed mechanism containing 310 species and 8011 reactions and describing the pyrolysis, partial oxidation, and combustion of hydrocarbon fuels up to $C_{16}$
  - Xylene isomers are not differentiated

- Gail and Dagaut (2007) model from CNRS
  - Detailed mechanism for the combustion of m-xylene and composed of 189 species and 1359 reactions

- Modeling was evaluated in Chemkin 4.1 (Kee et al., 2006) using the Plug Flow Reactor subroutine with isothermal conditions
  - Step size of 0.5 cm from 0 to 40 cm and velocity of 333.3 cm/s
  - Models evaluated from 600 to 840 K at 10 K intervals
Experiment and Modeling Roadmap

• Neat xylenes under lean equivalence ratios in the PFR and the research engine

• Binary mixtures of xylenes and n-alkanes in the PFR and the research engine

• Different xylene isomers in JP-8 surrogates in the PFR and the research engine
Neat Xylene Oxidation Experiments & Modeling

- o-Xylene and m-xylene were each tested neat in the PFR, and reactivity was not observed as there was no production of CO and CO$_2$ and no reduction of O$_2$
  - Experimental conditions were 600-825 K temperatures, 8 atm pressure, 120 ms residence time, fuel molar fraction $\sim 0.00120$ (1200 ppm), $\phi \sim 0.30$

- Neat o-, m-, and p-xylene were each tested in the research engine, and reactivity was not observed as the in-cylinder pressure traces matched a motored run

- The Ranzi model predicted no reactivity for neat xylene and the Dagaut model predicted no reactivity for neat m-xylene, over the experimental temperature range of 600-840 K
  - Ranzi model predicted reactivity at 850 K and higher, producing several aromatic species (phenol, benzoquinone, benzaldehyde, phenylmethanol, and cresol)
Xylene / n-Dodecane Oxidation in the PFR

77% n-dodecane / 23% xylene by liquid volume

Pressure: 8 atm

Residence time: 110 ms

Equivalence ratio: 0.23

Fuel molar fraction ~ 0.00046
(295 ppm n-dodecane / 165 ppm xylene)

O₂ molar fraction ~ 0.032

N₂ molar fraction ~ 0.97

CO from (- - -): o-xylene mixture, (—): m-xylene mixture
n-Dodecane / DX Blend / Scaled n-Dodecane

Pressure: 8 atm
Residence time: 110 ms
Equivalence ratio: 0.23

- No significant effect on CO production from xylene was observed

CO from (——): n-dodecane, (⋯⋯): 77% n-dodecane / 23% m-xylene,
(- - -): calculation for 77% n-dodecane / 23% non-reactive species
Xylene / n-Dodecane & JP-8 in the PFR

- 77% n-dodecane / 23% m-xylene surrogate has been proposed by the Jet Fuel Surrogate Working Group to match JP-8 sooting formation
  - Highlights the difficulties in tuning surrogates for different targets

Pressure: 8 atm
Residence time: 110 ms
Equivalence ratio: 0.23

(—): CO from 77% n-dodecane / 23% m-xylene; (- - -): CO from JP-8 #3773, considered to be a sample of “average” reactivity and composition
Kinetic Modeling

(—): CO (E), (●): CO (M), (- -): CO₂ (E), (▲): CO₂ (M)

- Ranzi model predicted results for 77% n-dodecane / 23% o-xylene well considering that the xylenes were lumped and no modifications to the model were made for this study; but predicted reactivity at T>800 K

- Modeled as isothermal, but experiment has ~35 K temperature rise
p-Xylene / n-Dodecane Oxidation in the PFR

77% n-dodecane / 23% xylene by liquid volume
Pressure: 8 atm
Residence time: 120 ms
Equivalence ratio: 0.30
Fuel molar fraction ~ 0.0008
(516 ppm n-dodecane / 284 ppm xylene)
O₂ molar fraction ~ 0.042
N₂ molar fraction ~ 0.96

- Fuel molar fraction was increased for this p-xylene experiment ~2x over the o- and m-xylene experiments, to help with species identification
Species Identification

- Over 30 intermediates were identified from each of the 77% n-dodecane / 23% (m- / o- / p-)xylene experiments
  - Identification of linear alkenes, saturated and unsaturated aldehydes, ketones and cyclic ethers agreed with past n-dodecane work
  - o-, m-, and p-Tolualdehyde were identified in o-, m-, and p-xylene experiments, respectively
  - Toluene was identified in each experiment
  - p-Cresol was identified in p-xylene experiment

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Note: Sample collected at 837 K without O₂ to calibrate fuel and check for cracking
DX = 85% n-decane / 15% xylene by liquid volume

- DX with o-xylene showed slightly enhanced reactivity, with onset of combustion at 333 CAD, 1 CAD sooner than other mixtures

- Pressure rise above motored trace is driven by combustion energy release
  - Fuel in air slightly reduces unreactive, isentropic in-cylinder T and P
Temperature Rise in the Engine due to Piston Motion

- Temperature rise (calculated) for isentropic compression of n-decane / xylene mixtures in air at engine conditions from IVC (t = 0 ms) to TDC (t = 32.2 ms), considering temperature-dependent heat capacity ratios of reactants
  - Calculations for all three isomers are identical
  - Specific heats for fuels derived from Draeger (1985) and Scott (1974)
- $T_{\text{max}, \Delta S=0, \text{Air/Fuel}} = 1007$ K (temperatures comparable to work of Emdee et al. (1990, 1991) in Princeton high temperature flow reactor)
  - As $T_{\text{max}, \Delta S=0, \text{Air}} = 1054$ K, fuel addition reduces $T_{\text{max}, \Delta S=0}$ by 47 K
- 330 CAD (25ms) at $T=805$ K; 340 CAD at 893 K; 350 CAD at 973 K
S6 = 15% xylene / 10% iso-octane / 20% methylcyclohexane / 30% n-dodecane / 20% n-tetradecane / 5% tetralin, by liquid volume; JP-8 #3773 has “average” composition and reactivity of JP-8

- S6 with o-xylene showed enhanced reactivity, with combustion onset at 339 CAD
- Results confirm using the original Violi surrogate of S6 with m-xylene
Key Oxidation Pathways of o-Xylene

Reactions identified in the high temperature work of Emdee et al. (1990) are also rate-controlling at preignition and autoignition conditions

- Production of 2-methylbenzaldehyde (o-tolualdehyde) and toluene dominant at lower temperatures
- Isomerization of styrene from 5,6-bis(methylene)cyclohexa-1,3-diene (o-xylylene) at higher temperatures enhances reactivity of o-xylene
- Other high temperature paths are production of naphthalene, o-methylbenzyl alcohol, and o-ethyltoluene from 2-methylbenzyl radical (o-xylyl radical)
Key Oxidation Pathways of m-Xylene

- Reactions identified in the high temperature work of Emdee et al. (1991) are also rate-controlling at preignition and autoignition conditions
  - Production of 3-methylbenzaldehyde (m-tolualdehyde) and toluene dominant at lower temperatures
  - 3-Methylbenzyl radical (m-xylyl radical) does not produce m-xylylene
  - At high temperatures, 3-methylbenzyl radical produces other alkylated aromatics maintaining the m-xylene structure (m-ethyltoluene and m-methylbenzyl alcohol)
Key Oxidation Pathways of p-Xylene

- Reactions identified in the high temperature work of Emdee et al. (1991) are also rate-controlling at preignition and autoignition conditions
  - Production of 4-methylbenzaldehyde (p-tolualdehyde) and toluene dominant at lower temperatures
  - 4-Methylbenzyl radical (p-xylyl radical) produces 3,6-bis(methylene)cyclohexa-1,4-diene (p-xylylene) at higher temperatures
  - p-Xylylene does not isomerize to styrene, but leads to other alkylated aromatics maintaining the p-xylene structure (Emdee et al., 1991)
ROP Analysis of Ranzi model

• Dominant xylene pathway, based on a rate-of-production (ROP) analysis of the Ranzi model for xylene in the 77% n-dodecane / 23% xylene mixture evaluated in the PFR at 700 K

• Phenol, the predicted stable product, was not observed in experiments (though p-cresol, or 4-methylphenol, was identified in the p-xylene experiment)
Highlights, Key Observations, and Conclusions

• The xylene isomers are not reactive neat at lean stoichiometry at the low temperature PFR and engine test conditions

• In binary mixtures with n-alkanes, the xylenes are reactive
  – In the PFR (low T and NTC), o-, m-, and p-xylene are indistinguishable
  – In the engine (at T > 800 K), o-xylene showed slightly more reactivity than m- or p-xylene
  – Given this behavior, “lumping” of the xylenes for modeling purposes is appropriate at preignition and autoignition conditions

• In modified S6 JP-8 surrogates, o-xylene is slightly more reactive than m- or p-xylene
  – However, the originally proposed S6 surrogate with m-xylene matches JP-8 autoignition better than the more reactive o-xylene

• The key preignition branching pathways of xylene lead to the production of tolualdehyde and toluene as the major stable intermediates
References


