The autoignition of jet fuels

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Motivation

- Fuel supply: heavy crude → fossil FT → HRJ → ?
- Fuel utilization: shift toward premixed and lean

Working premise:

- The design and optimization of future combustion-based propulsion and energy systems will be more reliant on knowledge of reaction kinetics than at present.
  - Increases in computational power will support the addition of more chemistry to CFD.
  - Presently, reaction kinetics modeling of high molecular weight fuels is at best semi-predictive.

- *Continued advances in experiments, theory, and modeling are needed to develop predictive reaction kinetics.*

Kinetic targets, including ignition delay, provide…

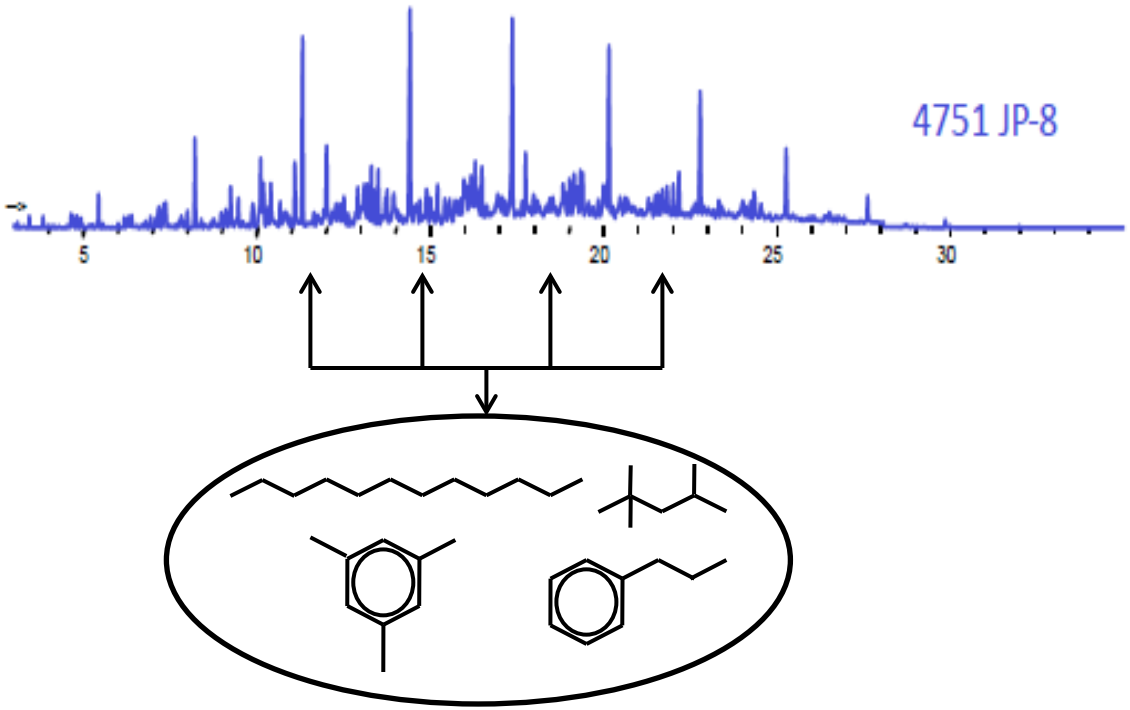
- Validation/assessment of kinetic models
- Direct insight into fuel chemistry
  - Structure-reactivity relationships
- Assessment of surrogates

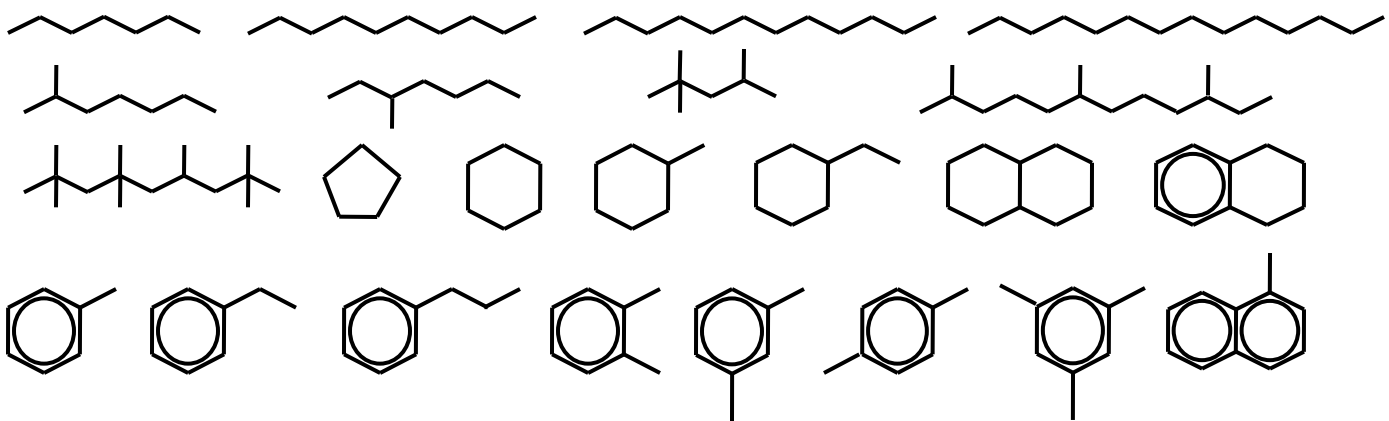
Kinetic targets *should* come from…

- Experiments in which transport processes are well-characterized performed at engine-relevant conditions
- e.g., shock tubes, rapid compression machines, flow reactors, flames, JSRs, etc.

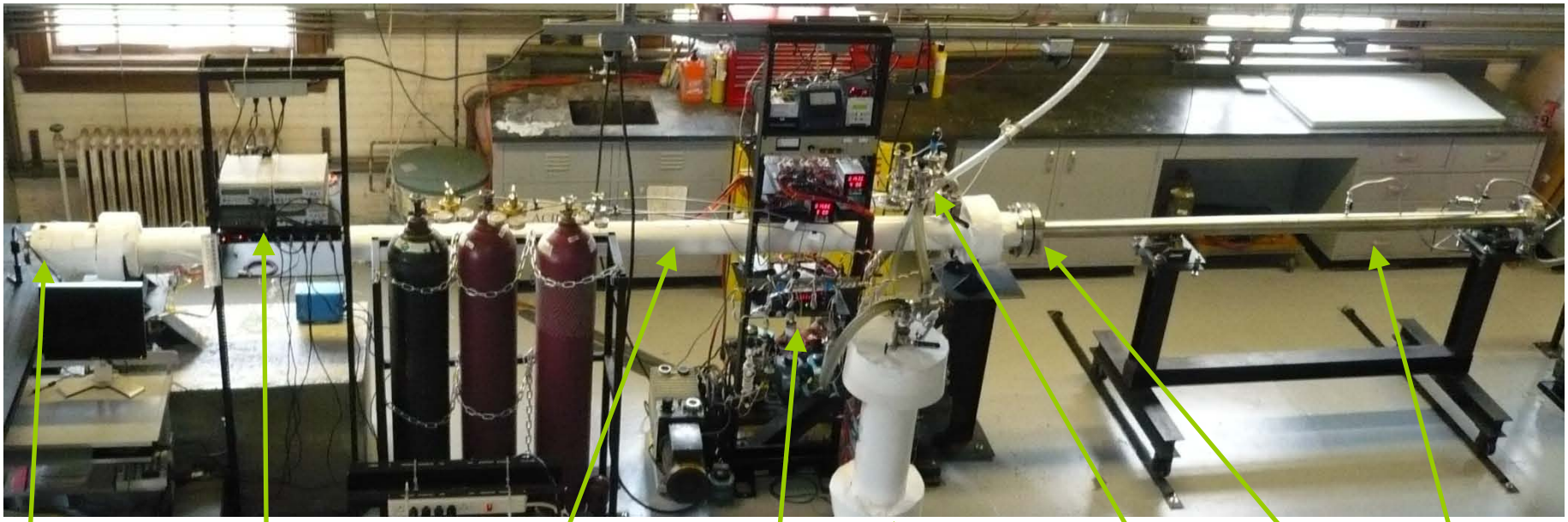
RPI jet fuel autoignition studies

- Shock tube studies for: real fuels, surrogates, and components





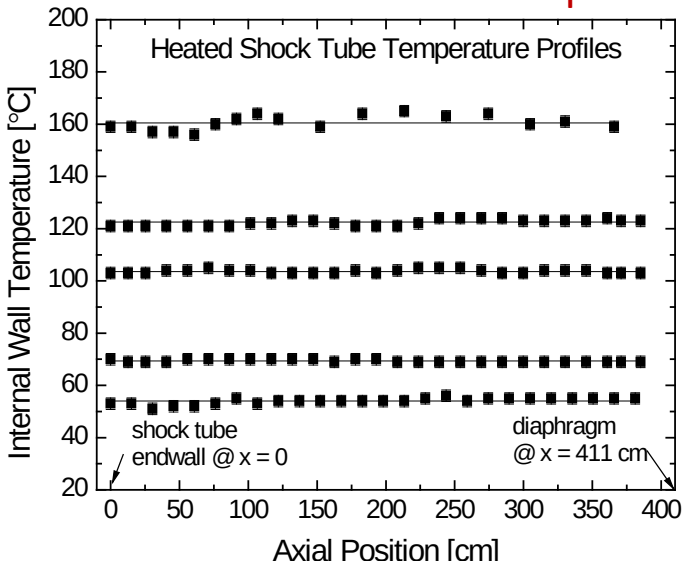
RPI shock tube facility



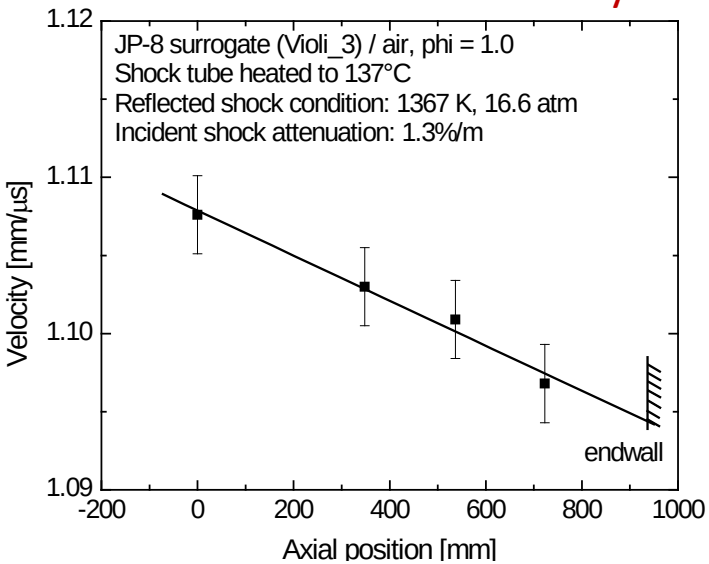
- Inner diameter = 5.7 cm
- Pressures up to 200 atm
- Initial temperatures up to 200°C
- Designed for kinetic studies of low vapor pressure fuels (jet fuels) at elevated pressures

Shock tube characteristics

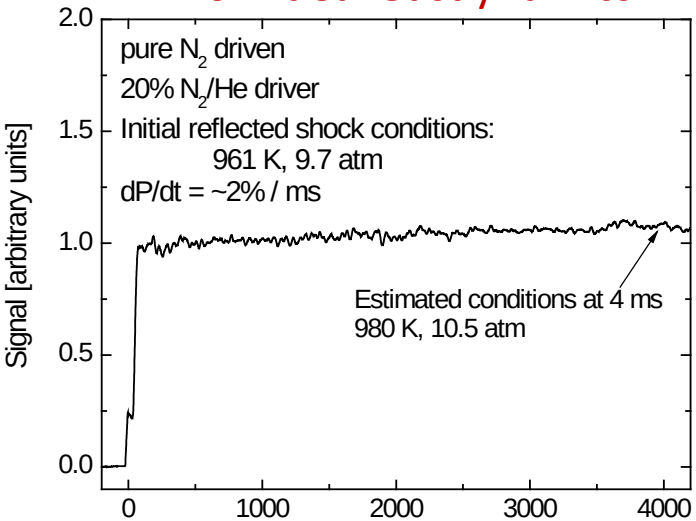
Heated Shock Tube Temperature



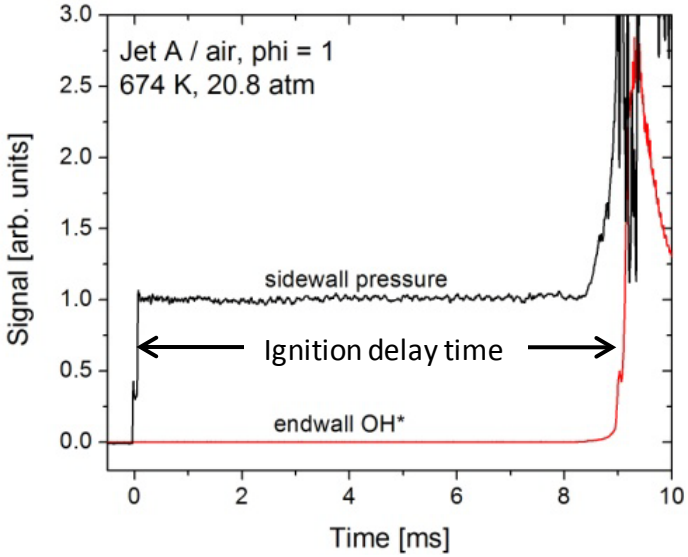
Incident Shock Velocity



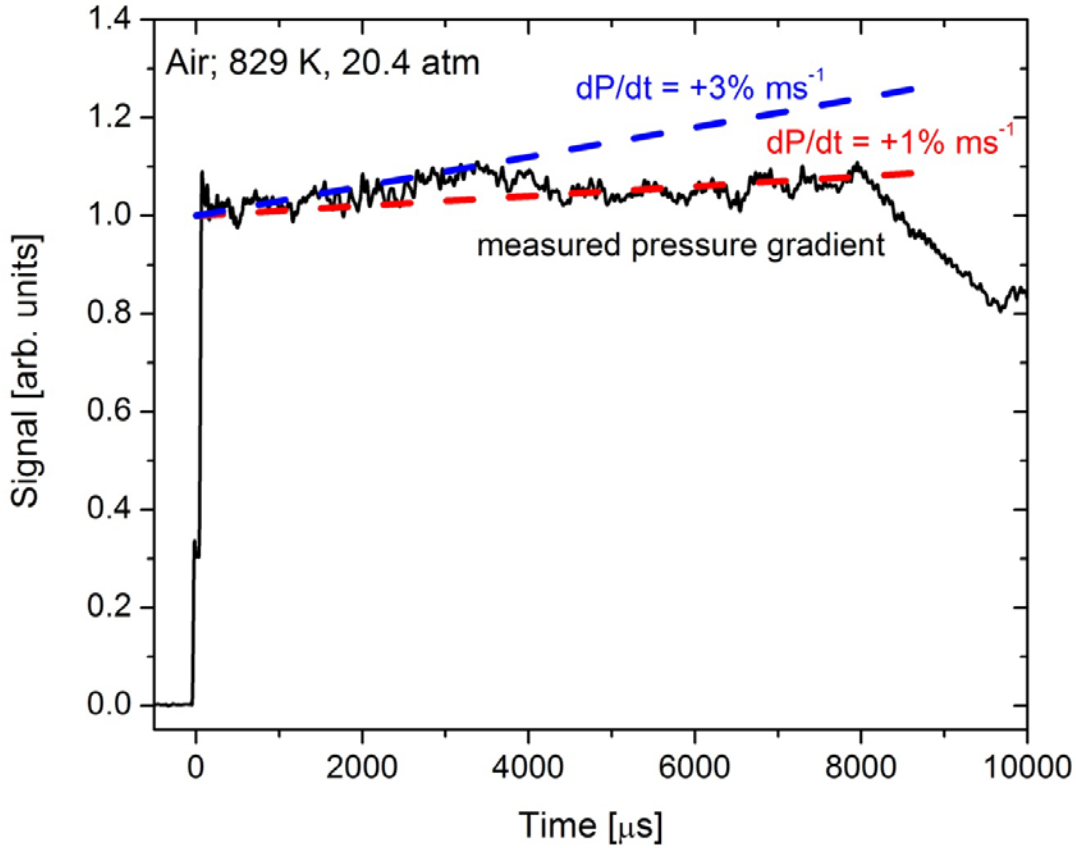
Non-Ideal Gasdynamics



Ignition Time Measurement



Non-ideal gasdynamic compression



- All reflected shock experiments exhibit some degree of non-ideal gasdynamic compression
- Measured pressure gradient: dP/dt = 1-3% ms^{-1}

➢ dP/dt can be included in modeling calculations by specifying a volume history (CHEMKIN)

Calculation of reflected shock conditions

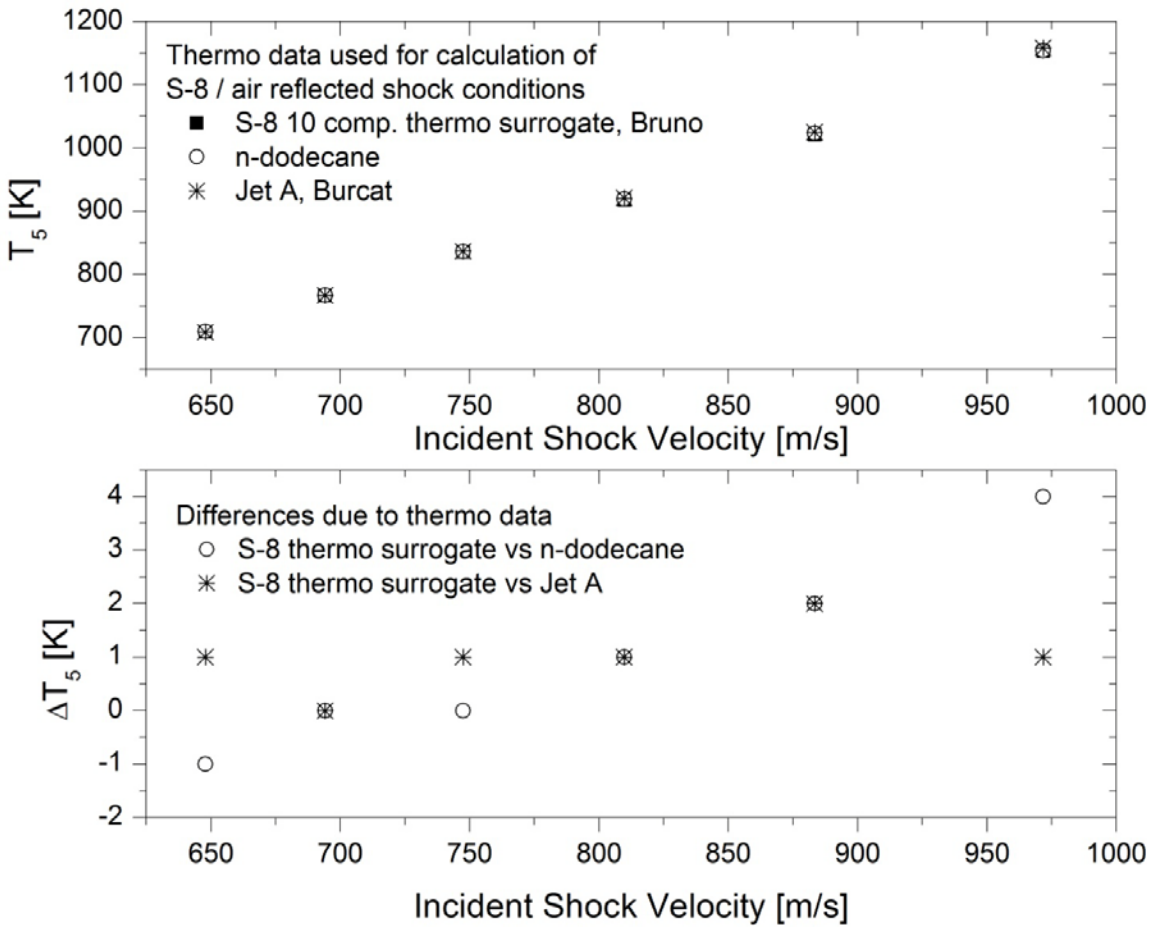
- Shock relations allow determination of post-shock conditions from measured incident shock velocity

- Requires a thermodynamic data
  - Specifies the specific heat ratio, Υ, in the normal shock relations

- For real fuels data may not exist
  - Can use a thermodynamic surrogate: may or may not be available in the literature

- Fortunately, the choice of the thermo surrogate has only a small influence on the reflected shock temperature

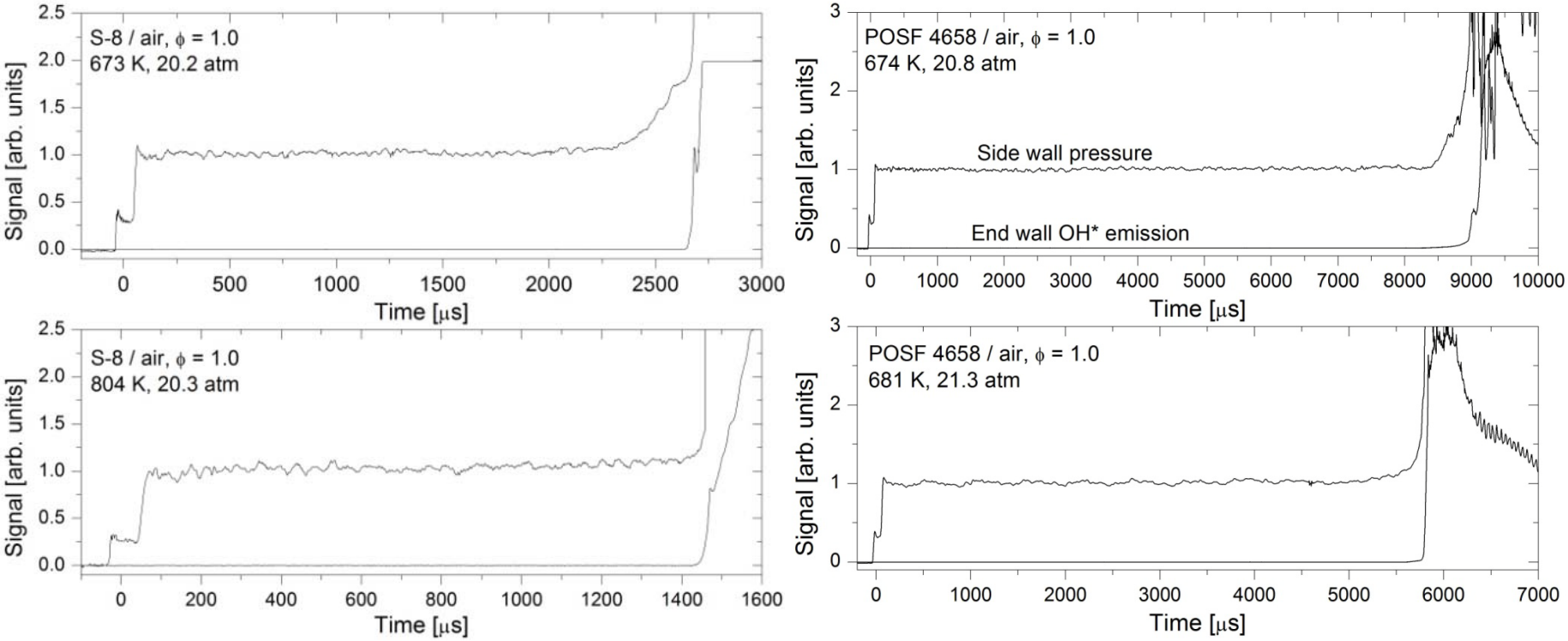
Thermodynamic sensitivity of T_5



- Reflected shock temperature varies by only 0-4 K for three vastly different thermo-dynamic surrogates

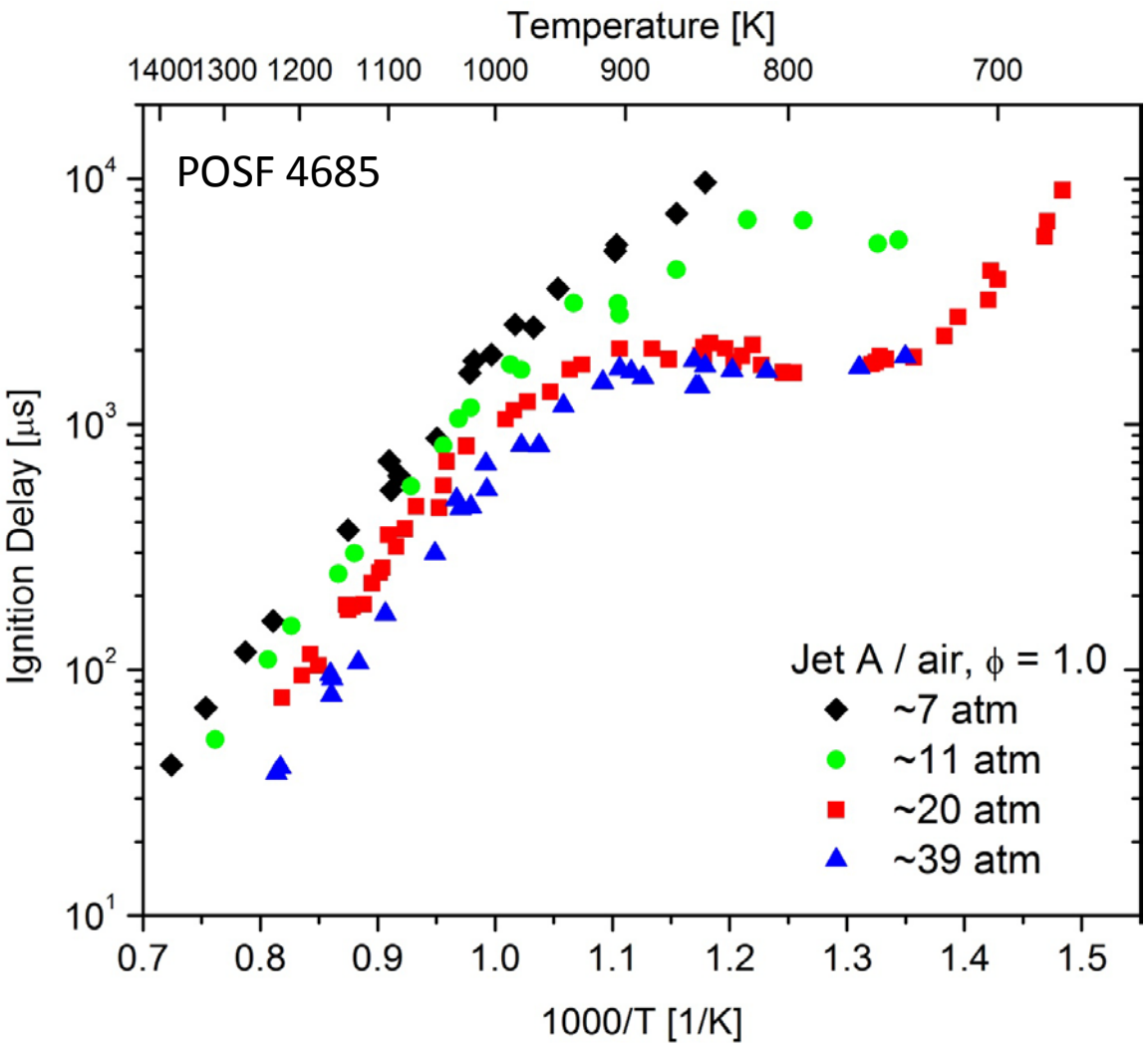
- Surrogate selection only influences the third decimal place in ϒ (ϒ = 1.39x)

Ignition delay pressure profiles



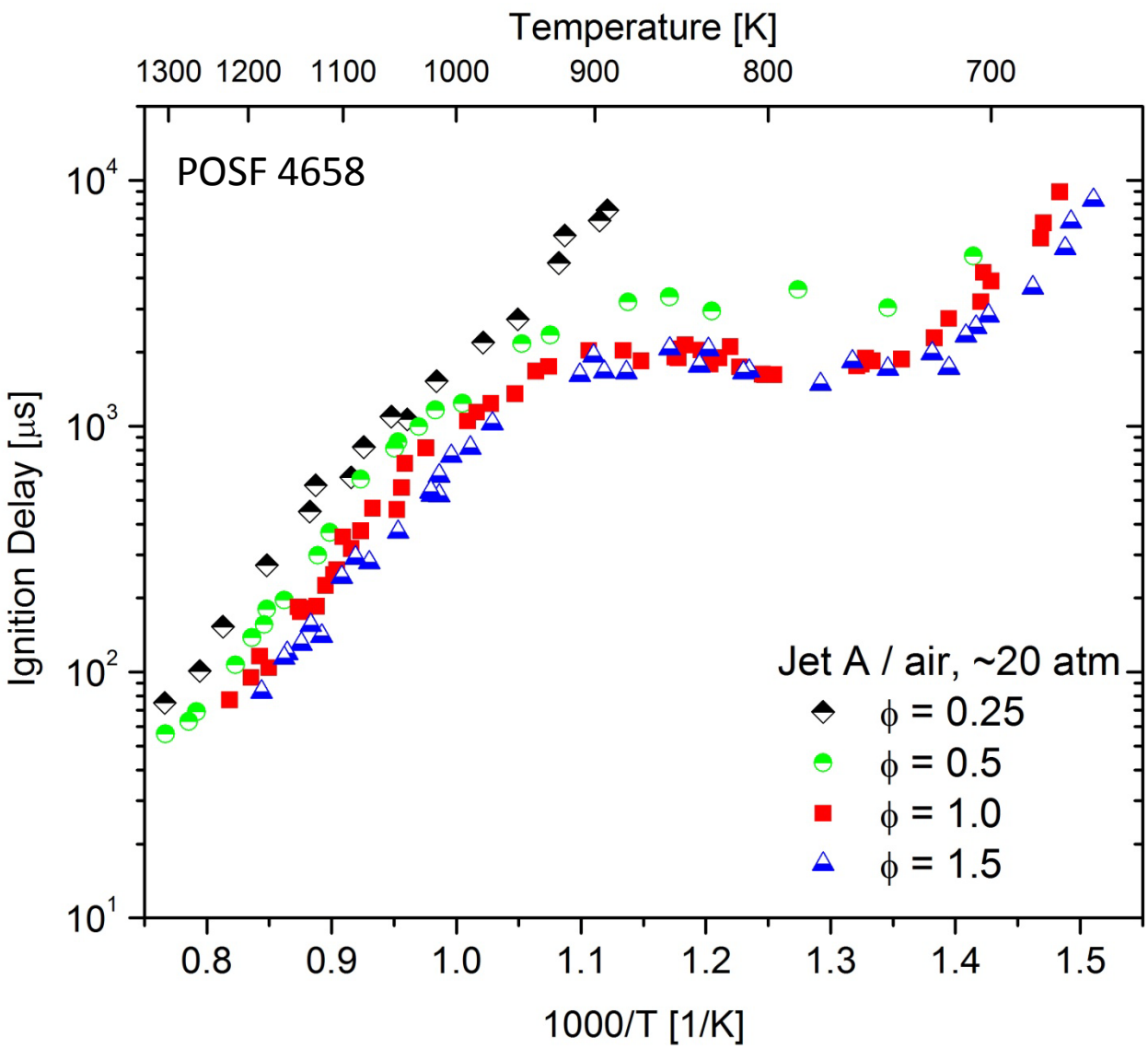
- Well behaved pressure profiles for <10 ms with N_2/He tailored driver gases
- Gasdynamic pressure rise (typically 2-3%/ms)
- Ignition is "strong" at all conditions: rapid pressure rise
  - In contrast to RCM experiments which under some conditions show distinct two-stage ignition: topic of current inquiry

Jet A ignition delay results: *P*-dependence

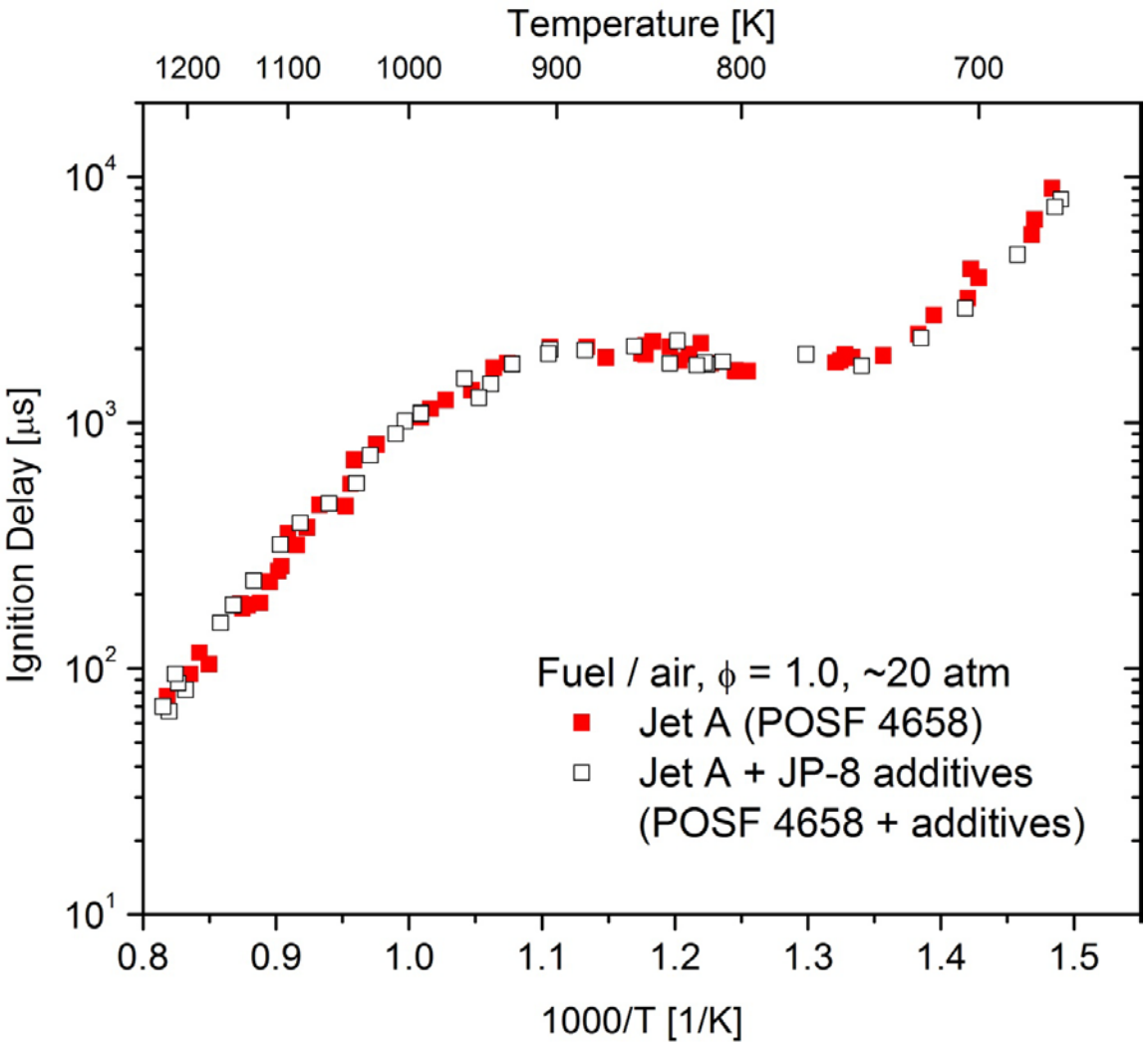


- Jet A (POSF 4658) ignition delay times
  - 7-39 atm
  - ϕ = 0.25, 0.5, 1.0, 1.5
  - 675-1400 K
- Greatly extends the range of available data
- Some overlap with RCM conditions

Jet A ignition delay results: ϕ-dependence



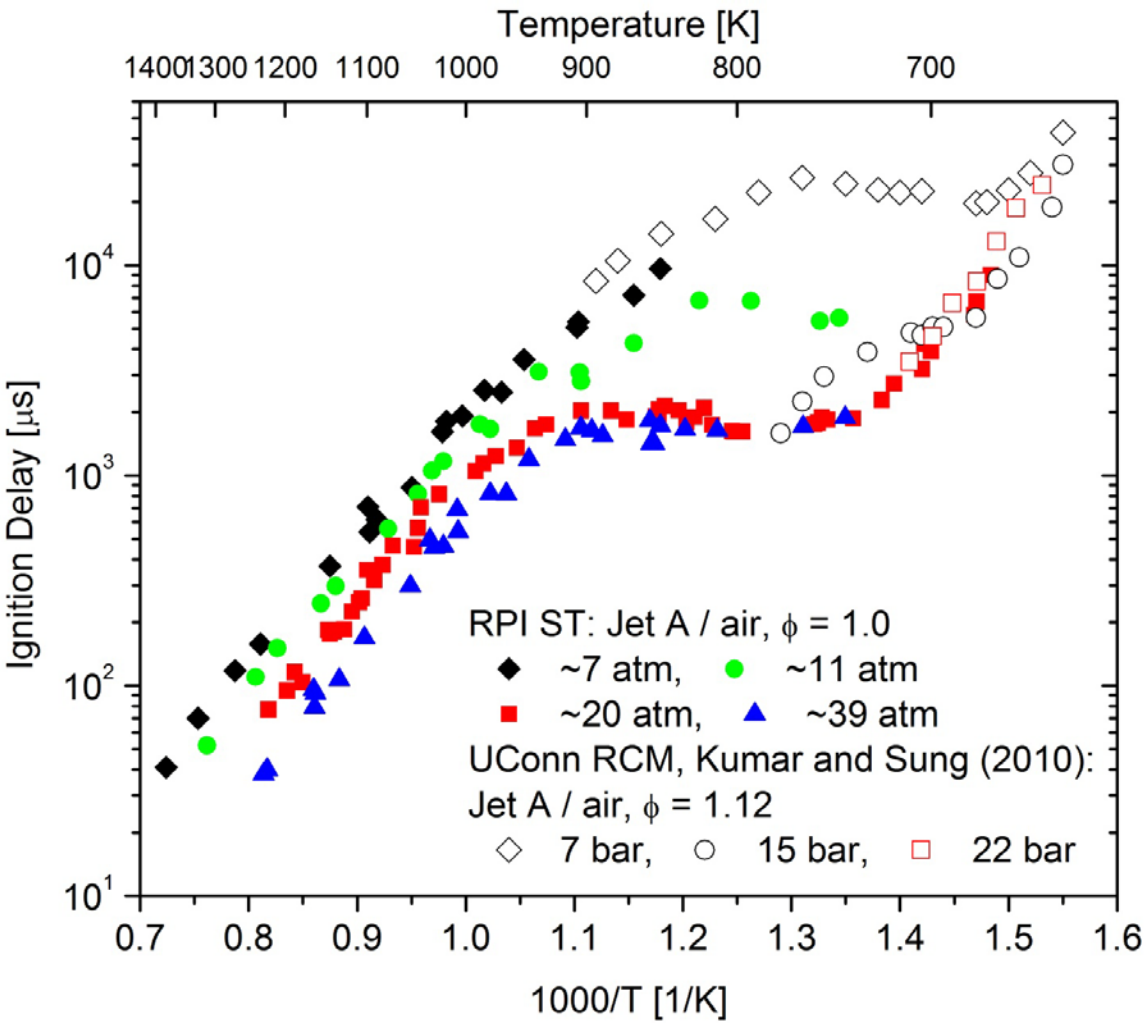
Influence of JP-8 additives



- No discernible influence of JP-8 additive package on ignition delay

Jet A experimental comparisons:

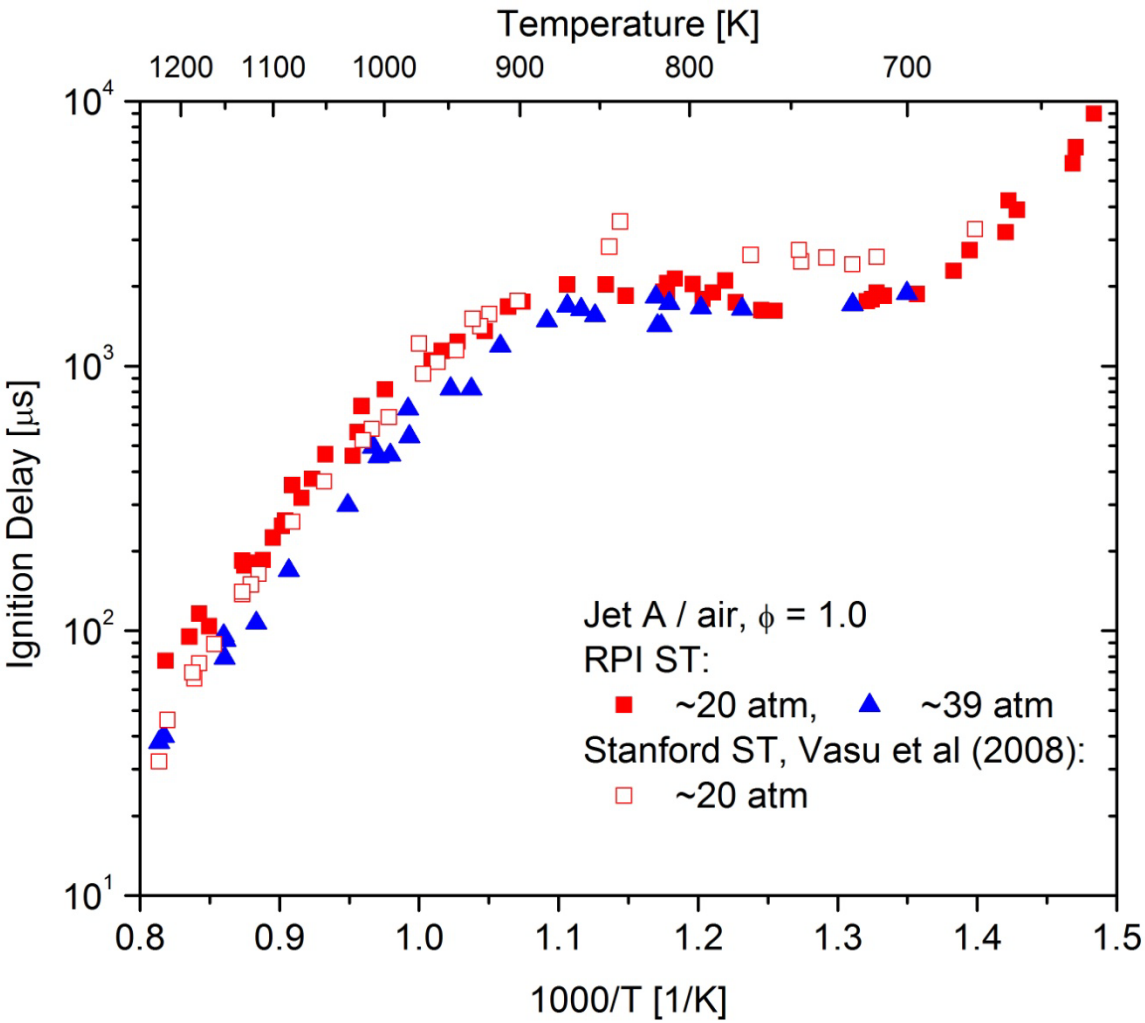
RPI ST vs UConn RCM



- Fairly good agreement with UConn RCM data
- Boundary conditions are different for these two experiments
- Observed pressure behavior is different: two-stage in RCM and single-stage in ST

Jet A experimental comparisons:

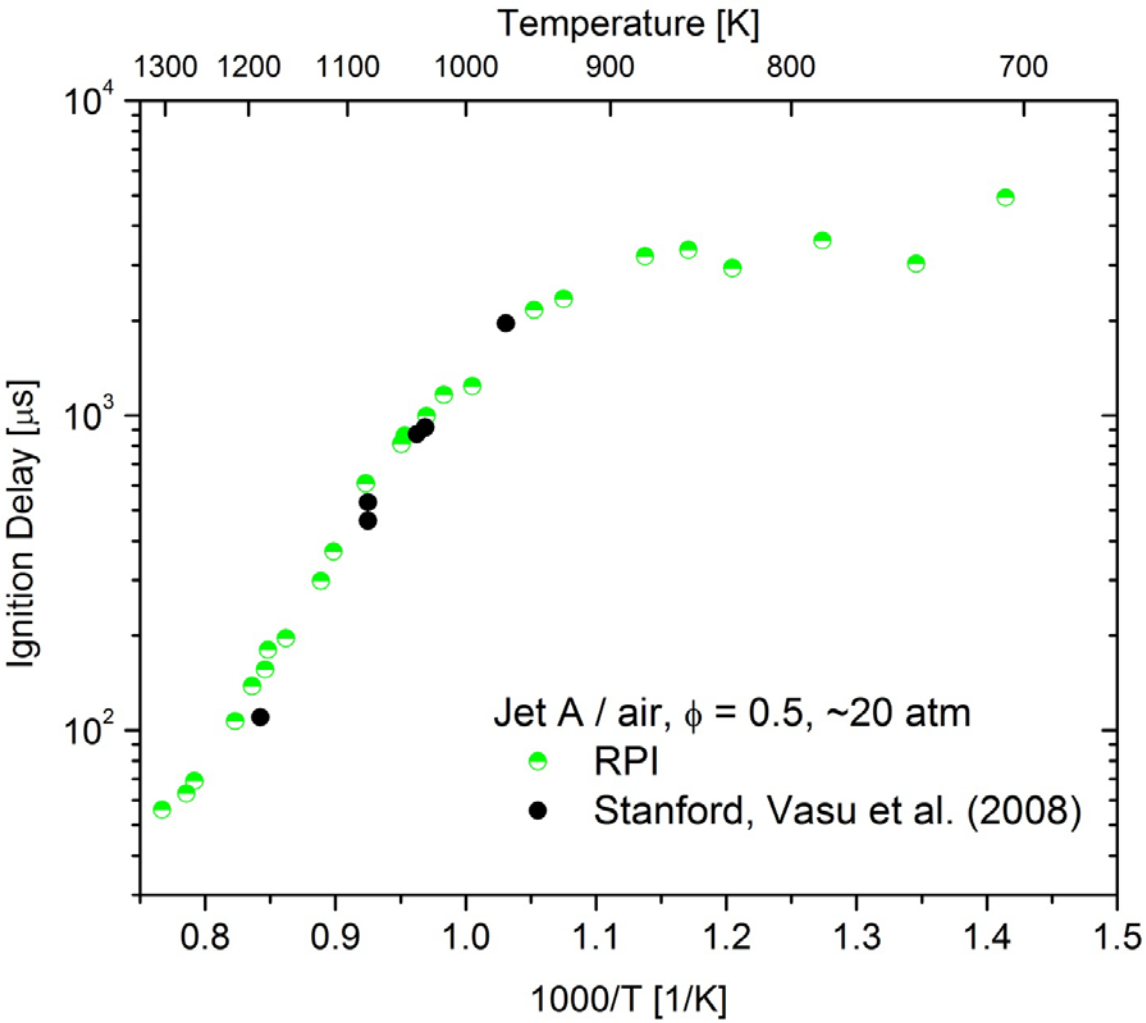
RPI ST vs Stanford ST (1/2)



- Good agreement with Stanford shock tube data at 20 atm and high T
- Deviation in the NTC of about a factor of 1.5
  - Different fuel fractions used to define ϕ = 1.0: 1.368% RPI and 1.276% Stanford

Jet A experimental comparisons:

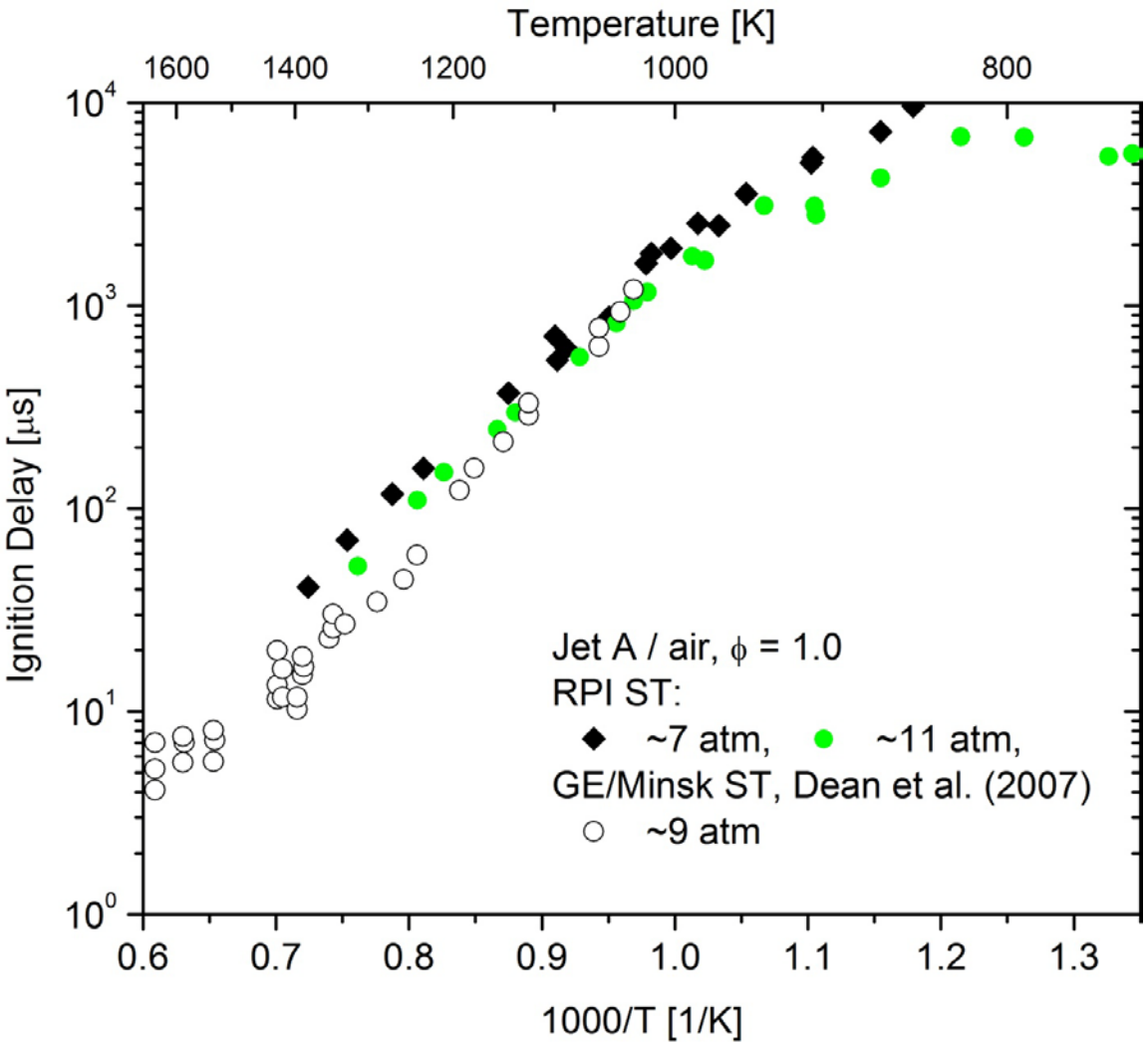
RPI ST vs Stanford ST (2/2)



- Good agreement with Stanford shock tube data at limited ϕ = 0.5 conditions

Jet A experimental comparisons:

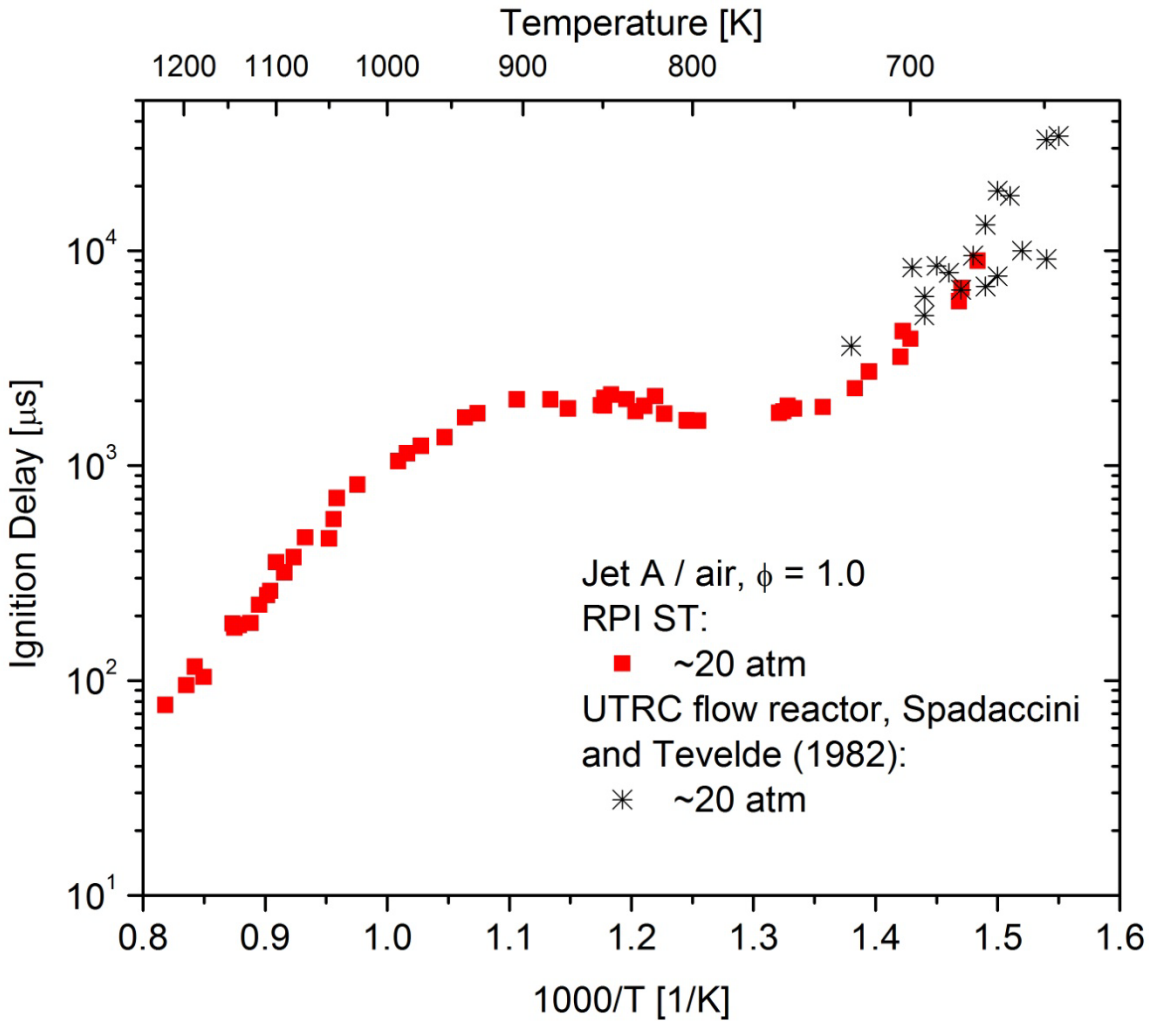
RPI ST vs GE/Minsk ST



- Good agreement with Dean et al. (2007) for T<1200 K
- Factor of two deviation from 1200-1400 K

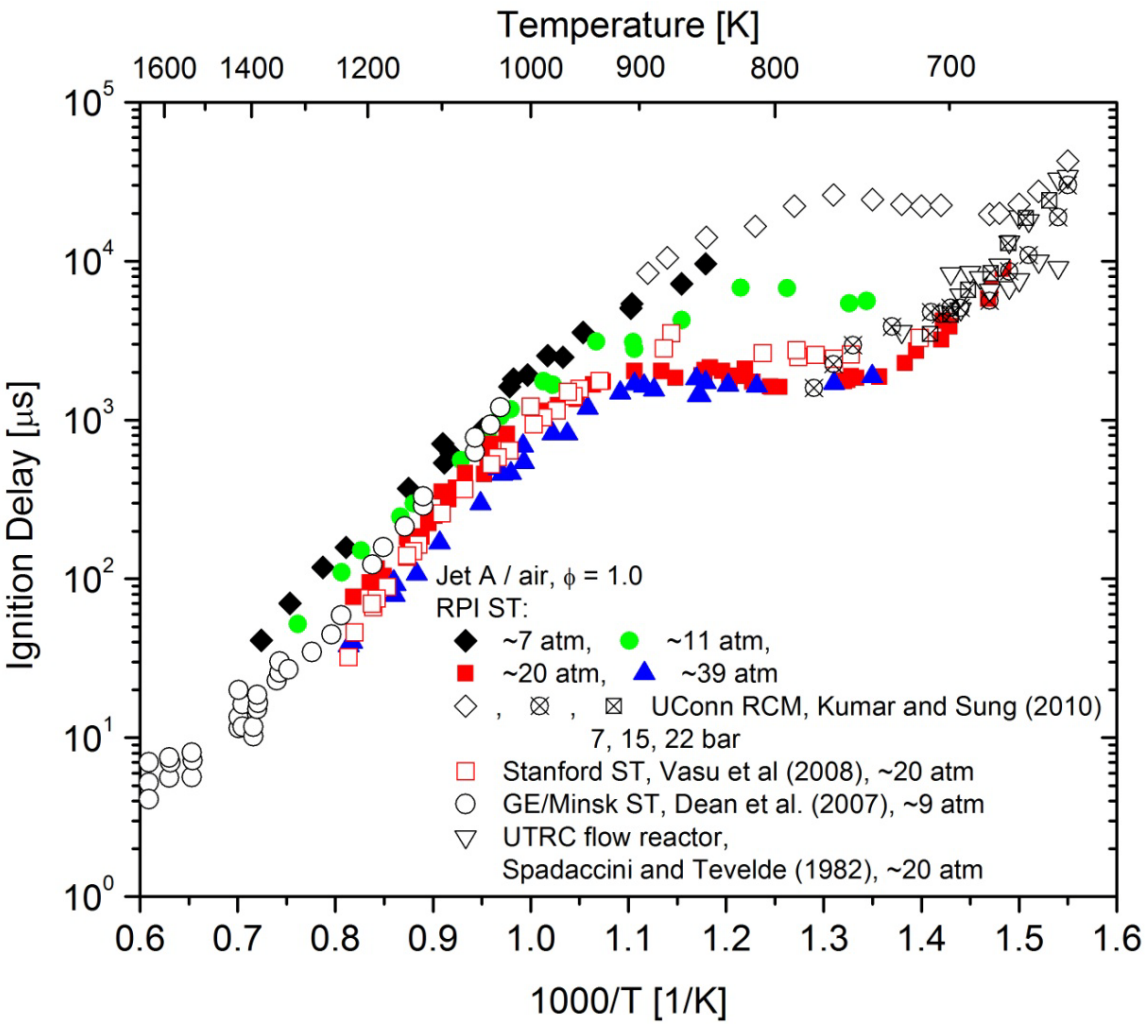
Jet A experimental comparisons:

RPI ST vs UTRC flow reactor



- Comparison with ignition in UTRC flow reactor (1982)
- Flow reactor data has large scatter but intersects with lowest temperature data from RPI ST

Jet A: summary



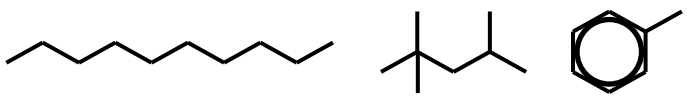
- Experiments from five groups: RPI, UConn, Stanford, GE/Minsk, UTRC
- Three distinct reactors: shock tube, RCM, flow reactor
- Data mostly agree within a factor of two

Jet A surrogate: MURI 1st-gen surrogate

Surrogate formulated by matching H/C and DCN

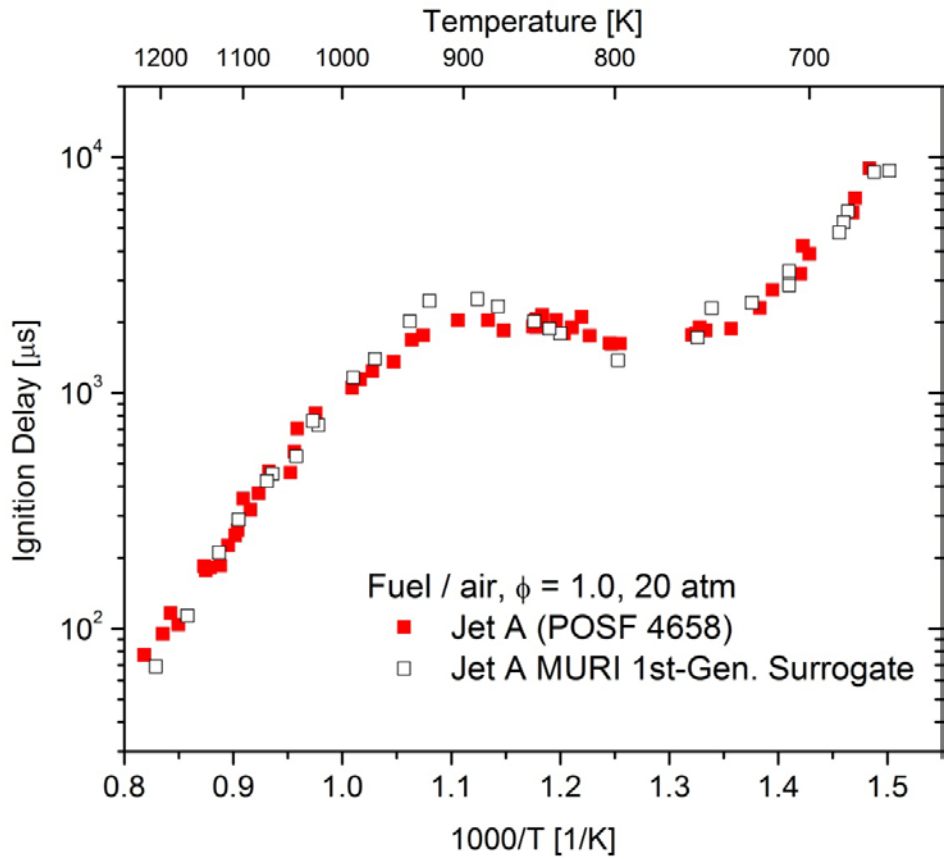
Surrogate component	molar-%
n-decane	42.67
iso-octane	33.02
toluene	24.31

Fuel	H/C	MW	DCN	TSI
Jet A (POSF 4658)	1.957	142	47.1	21.4
Surrogate	2.01	121	47.1	14.1

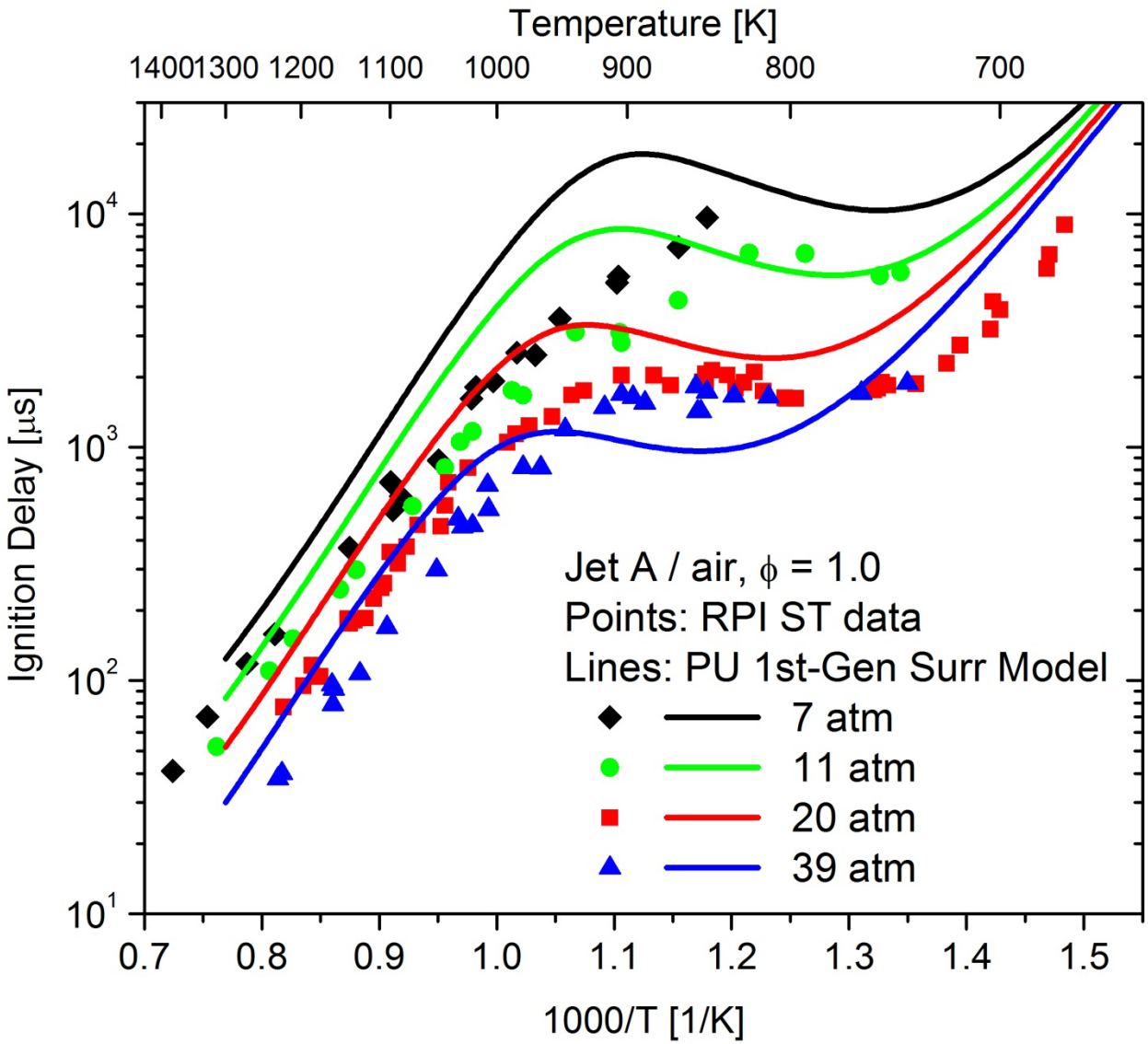


Surrogate validation:

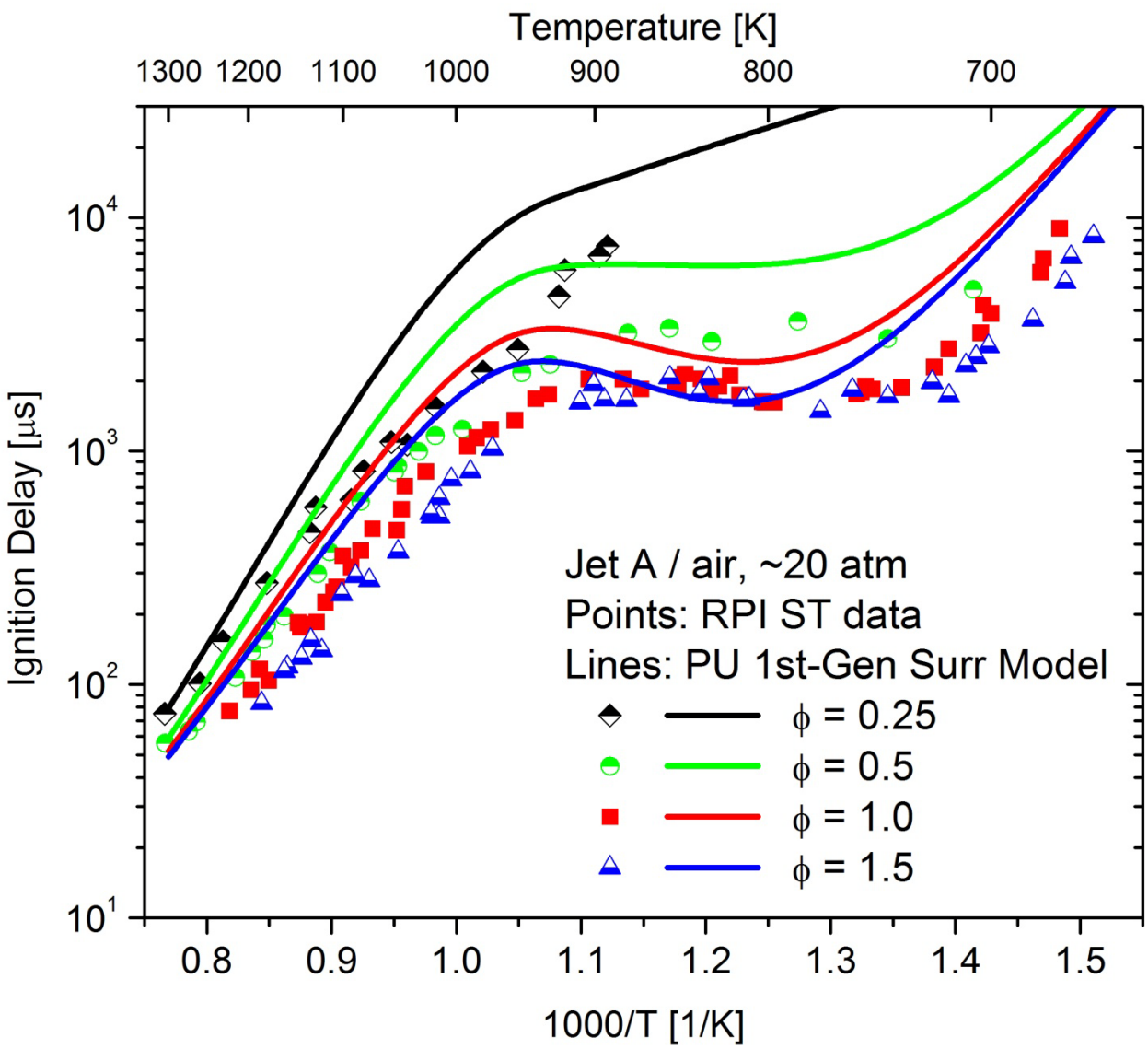
- Diffusive extinction
- Flow reactor reactivity/speciation
- Rapid compression machine and shock tube autoignition



Jet A vs surrogate modeling



Jet A vs surrogate modeling



Fischer-Tropsch fuels

Ignition delay experiments for three FT fuels: Syntroleum S-8, Shell FT, and Sasol IPK

Fuel	AFRL #	n-alkane	iso-alkane	cyclo-alkane	aromatic	other
Jet A (typical)	4658	28	29	20	18	5
S-8 (GTL)	4734	17	83			
Shell FT (GTL)	5172	42	57	1		
Sasol IPK (CTL)	5642	1.5	89	9.5		

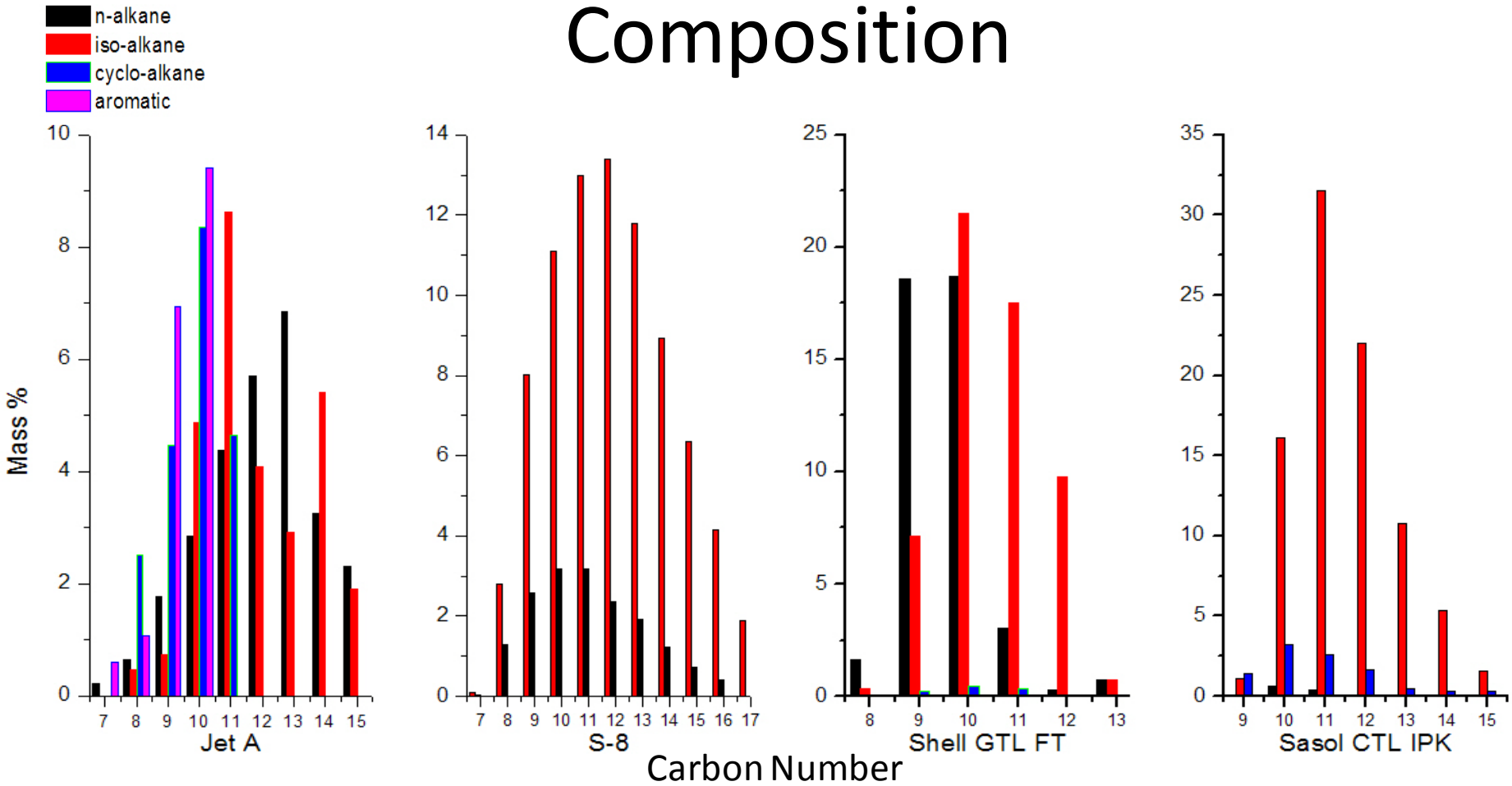
% by volume

Fuel	H/C	DCN*	Liq density [kg/m^3]	Avg MW [kg/kmol]
Jet A	1.84-2.07	30-60	~805	140-160
S-8 (GTL)	2.17	59	755	163
Shell FT (GTL)	2.2	60	736	148
Sasol IPK (CTL)	2.17	31	769	153

GTL – gas to liquid
CTL – coal to liquid

*DCN – derived cetane number

Composition

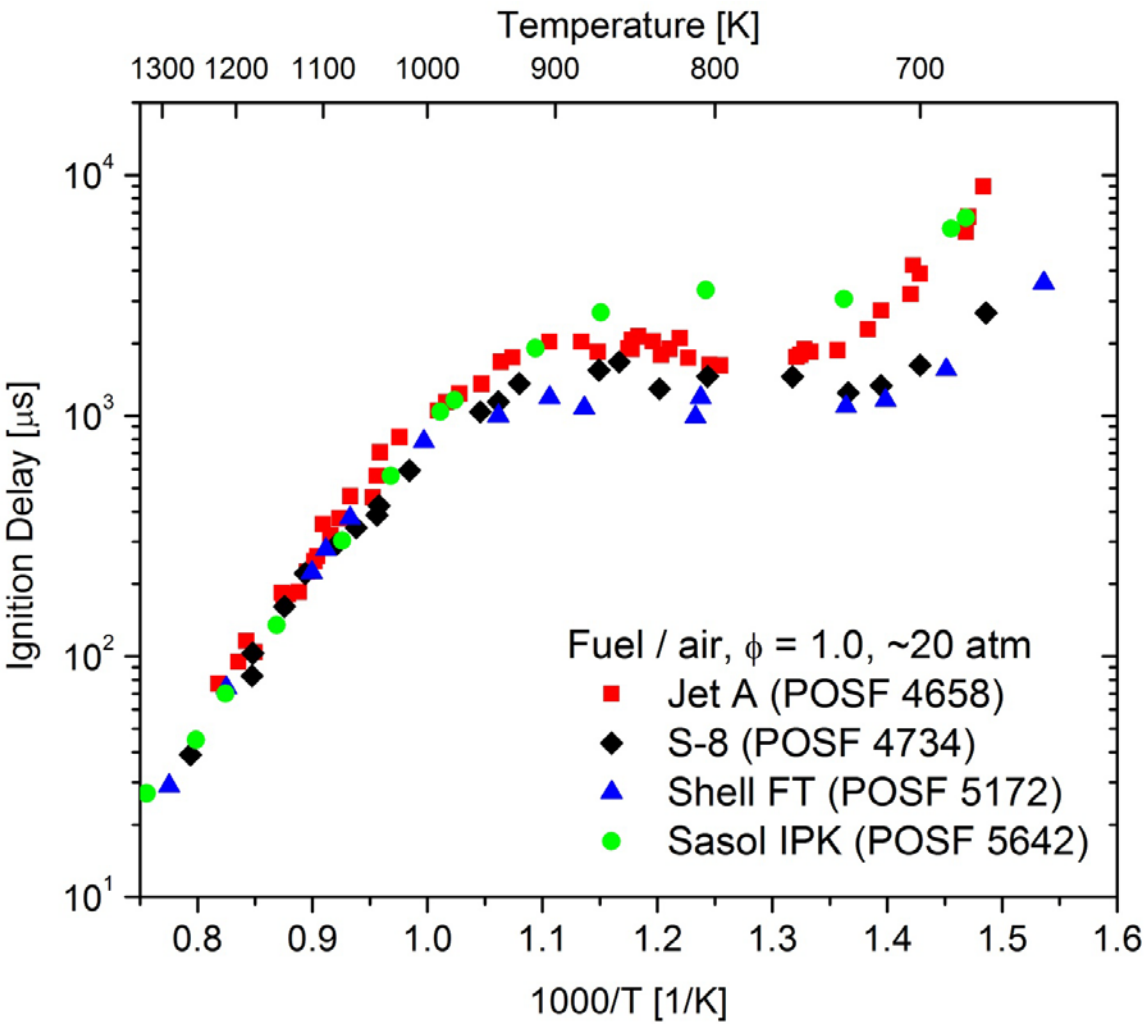


Composition variable in terms of:

1) Organic distribution
2) Average MW and width of MW distribution
3) Number of compounds

Fuel	n-alkane	iso-alkane	cyclo-alkane	aromatic
Jet A	28	29	20	18
S-8	17	83		
Shell FT	42	57	1	
Sasol IPK	1.5	89	9.5	

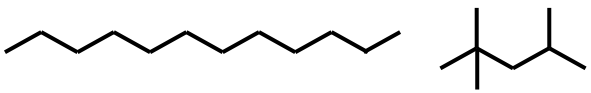
Fischer-Tropsch autoignition



- Similar high-T ignition delay
- Differences at low T
- Sasol IPK: 89% iso-alkanes, DCN = 31
- S-8: 17/83% n-/iso-alkanes, DCN = 59
- Shell FT: 42/57% n-/iso-alkanes, DCN = 60

S-8 surrogate

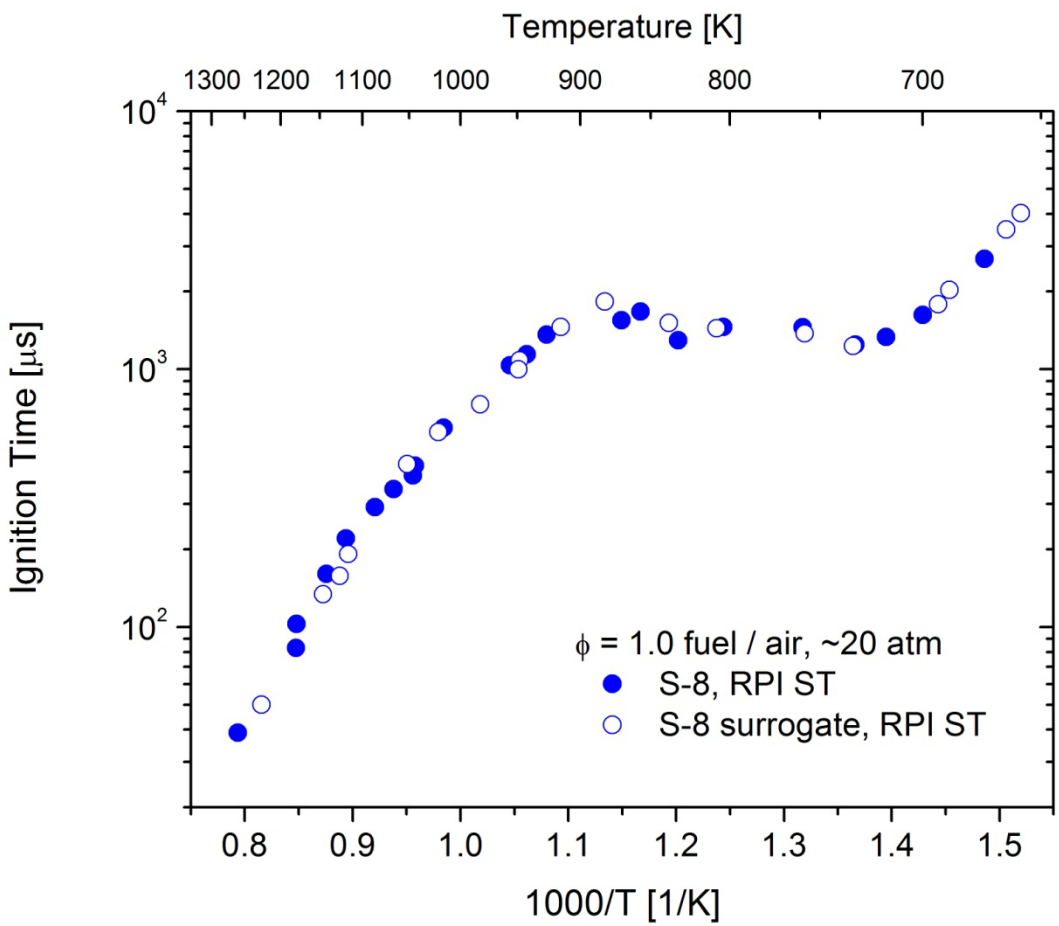
Surrogate component	molar-%
n-dodecane	51.9
iso-octane	48.1



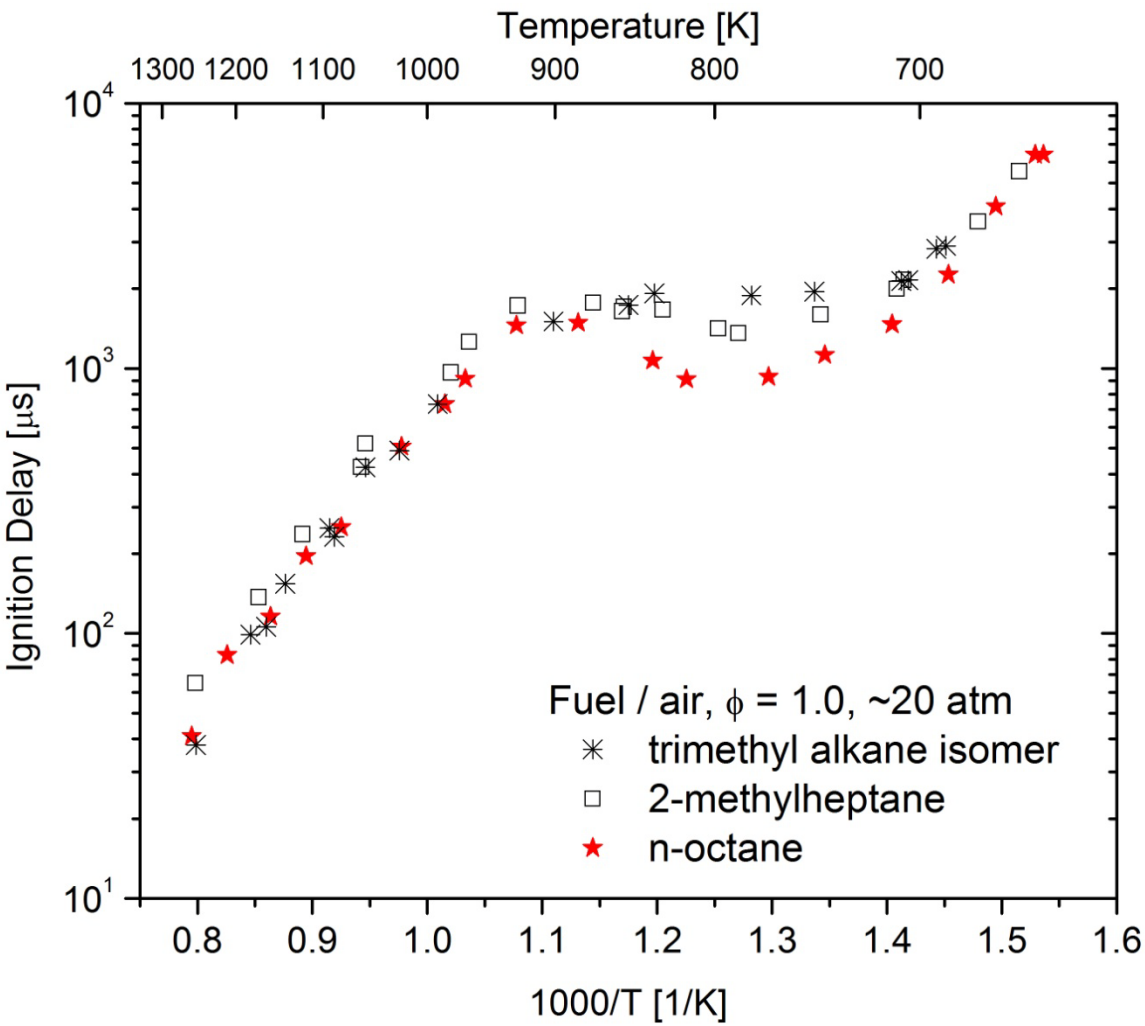
Fuel	H/C	MW	DCN	TSI
S-8 (POSF 4734)	2.17	163	58.7	n/a
Surrogate	2.19	143	58.9	n/a

Surrogate validation:

- Diffusive extinction
- Flow reactor reactivity/speciation
- Rapid compression machine and shock tube autoignition

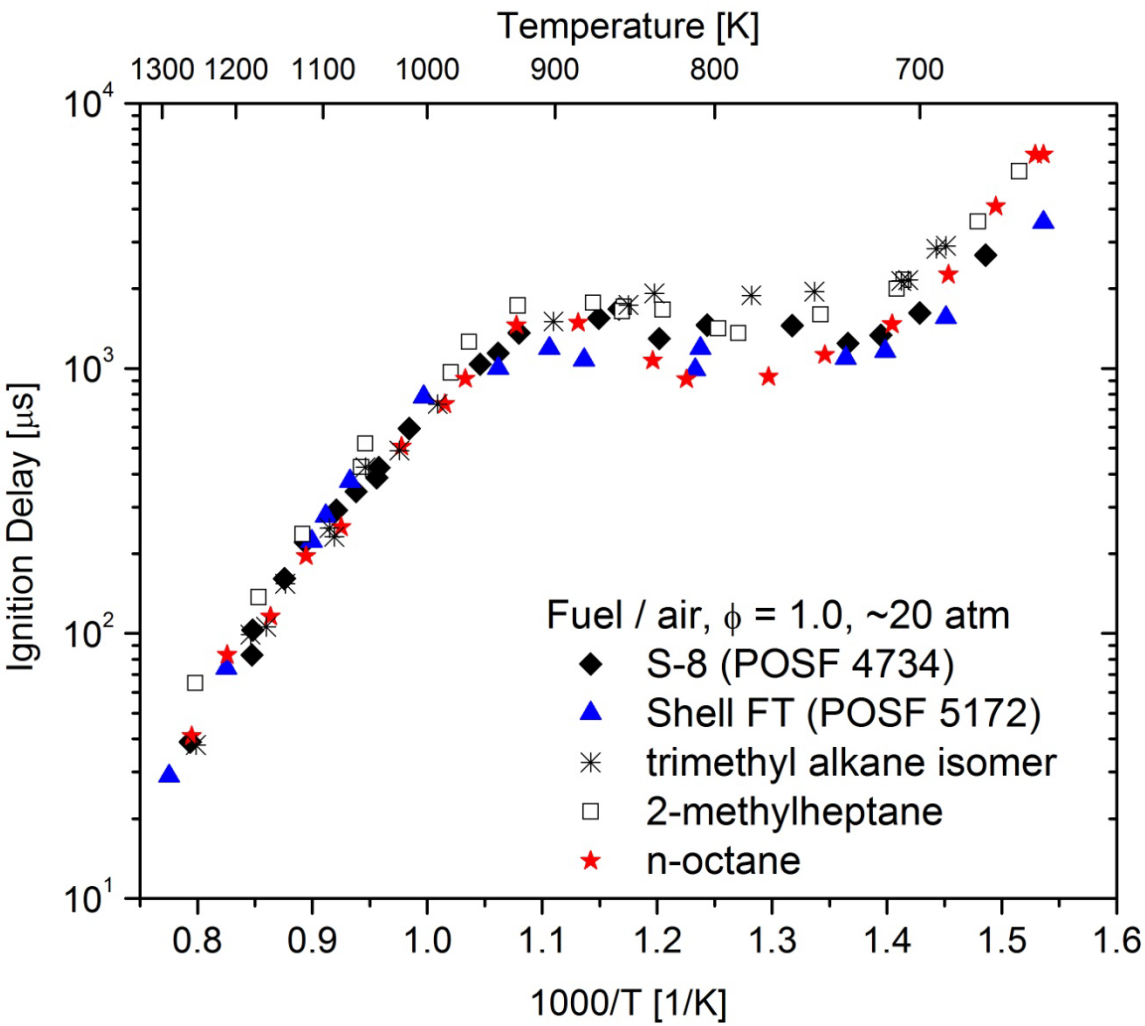


Alkanes



- Similar high-T ignition delay
- Differences in the NTC consistent with the number of potential RO_2 isomerization pathways

FT fuels vs alkanes

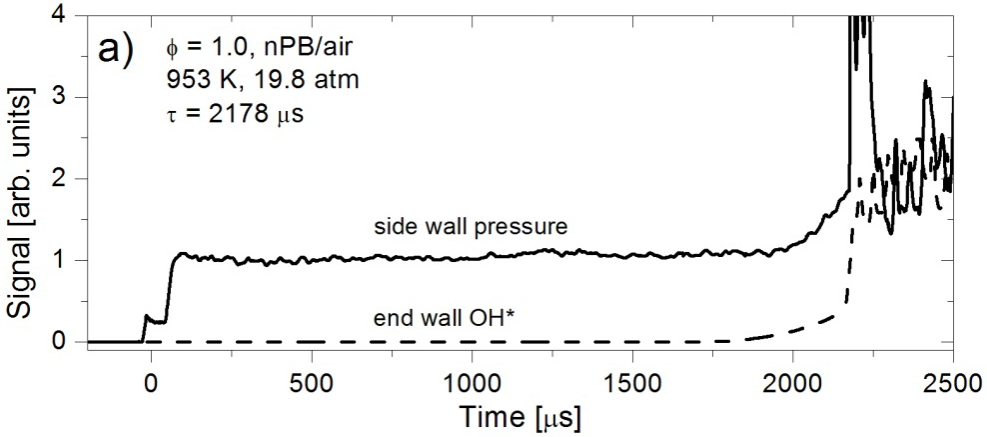


- S-8 is 83% and Shell FT is 57% iso-alkanes, most of which are lightly branched

Compound	DCN
S-8	59
Shell FT	60
2-methylheptane	52.8
n-octane	57.6

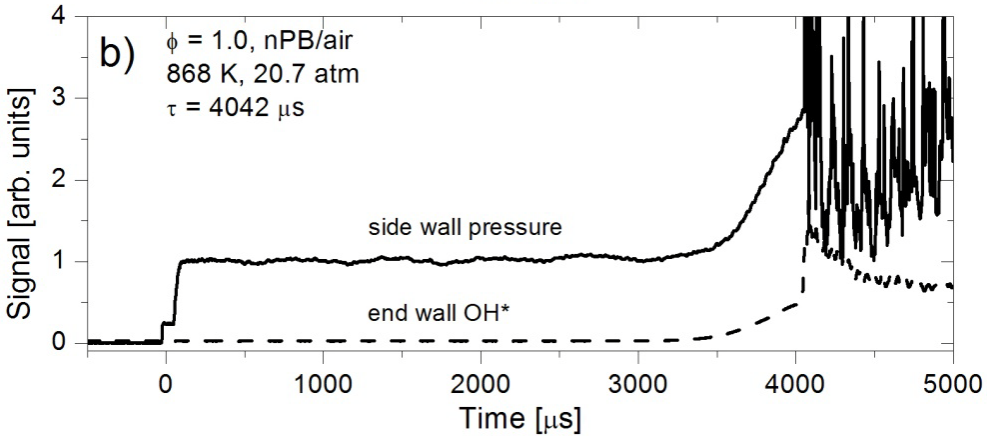
- Lightly branched alkanes as FT fuel surrogate components?

n-Propylbenzene – pressure traces



T > 950 K: strong ignition

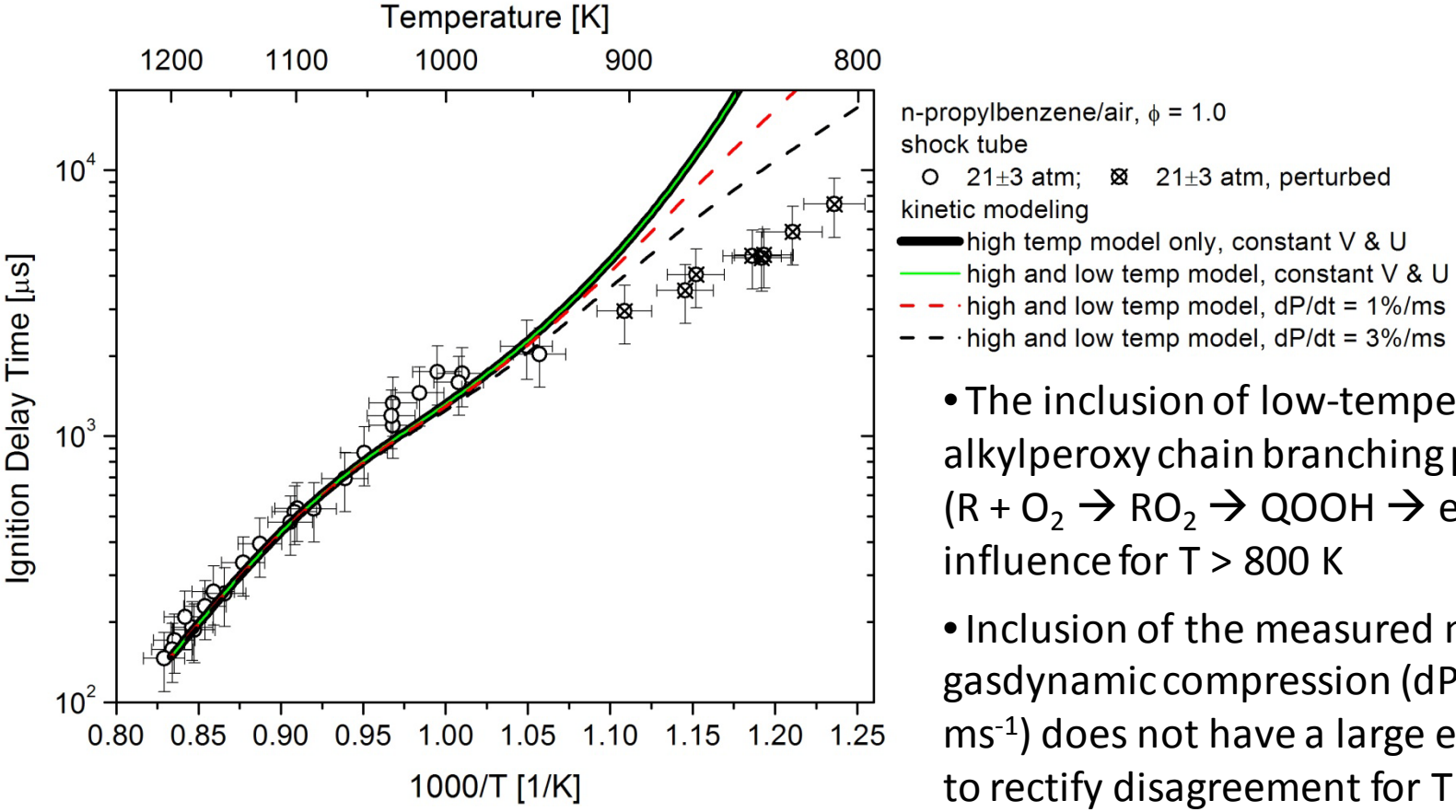
- little pre-ignition energy release



T< 950 K: mild ignition event prior to strong ignition (in some cases strong ignition does not occur)

- significant pre-ignition energy release
- inhomogeneous ignition

Low temperature deviations in exp vs model

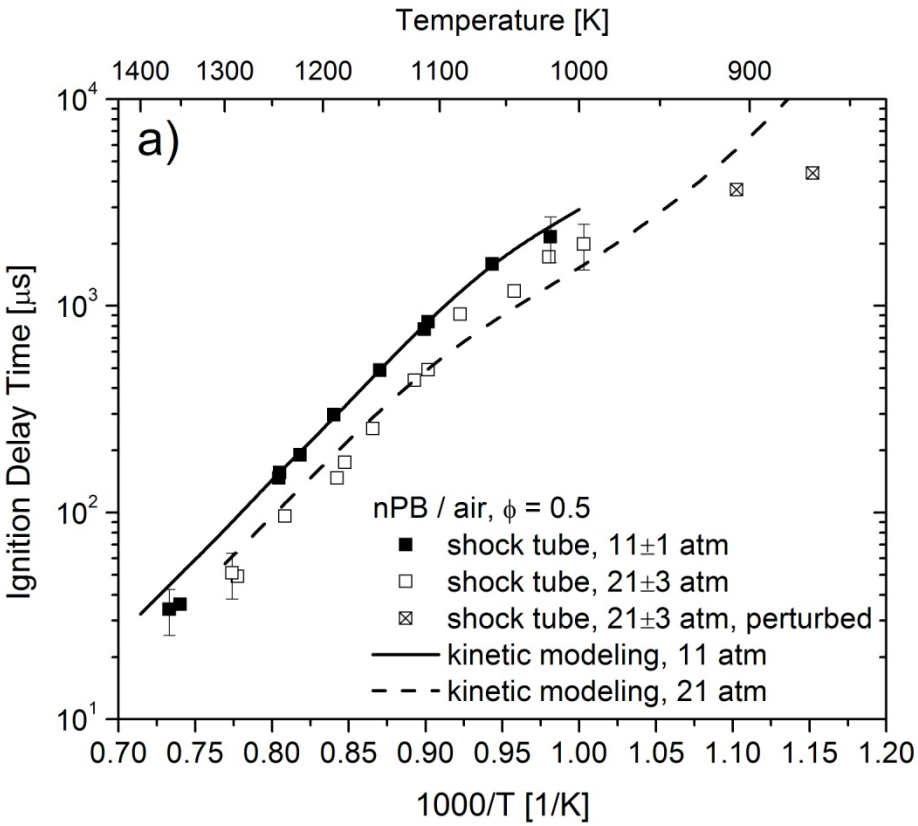


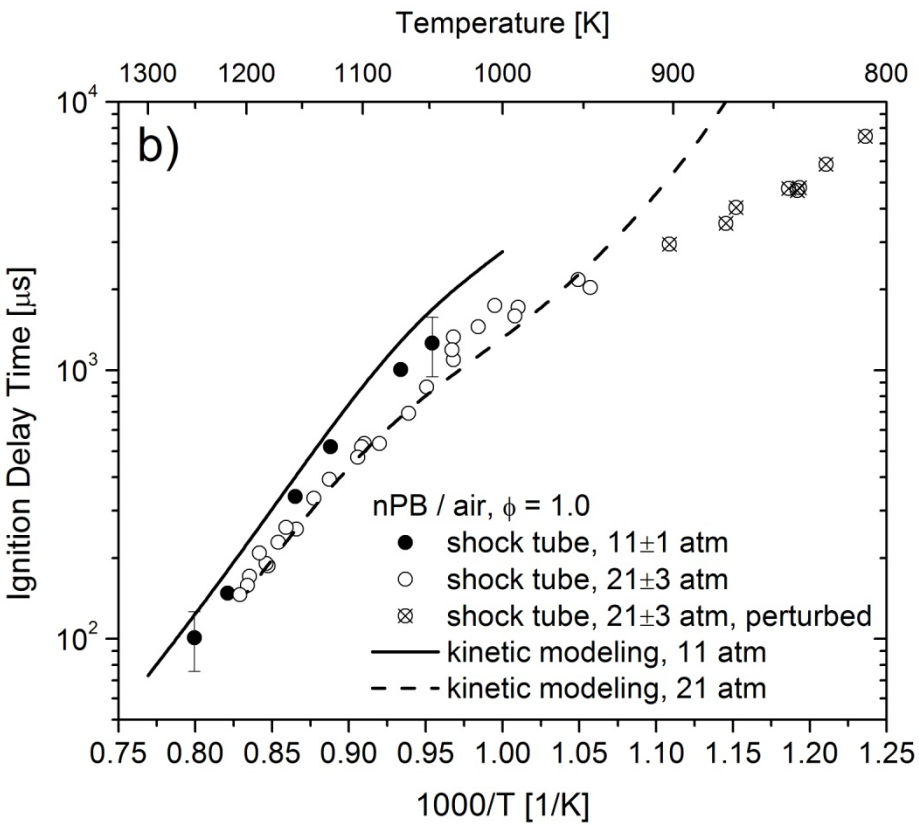
- The inclusion of low-temperature alkylperoxy chain branching pathway ($R + O_2 \rightarrow RO_2 \rightarrow QOOH \rightarrow$ etc) has no influence for T > 800 K
- Inclusion of the measured non-ideal gasdynamic compression (dP/dt = 1-3% ms^{-1}) does not have a large enough affect to rectify disagreement for T < 950 K

- Conclusion: inhomogeneous mild ignition observed in the pressure profiles significantly alters the measured ignition time
- Boundary conditions for modeling this process are ill defined

➢ Recommend not using such data for validation of kinetic models

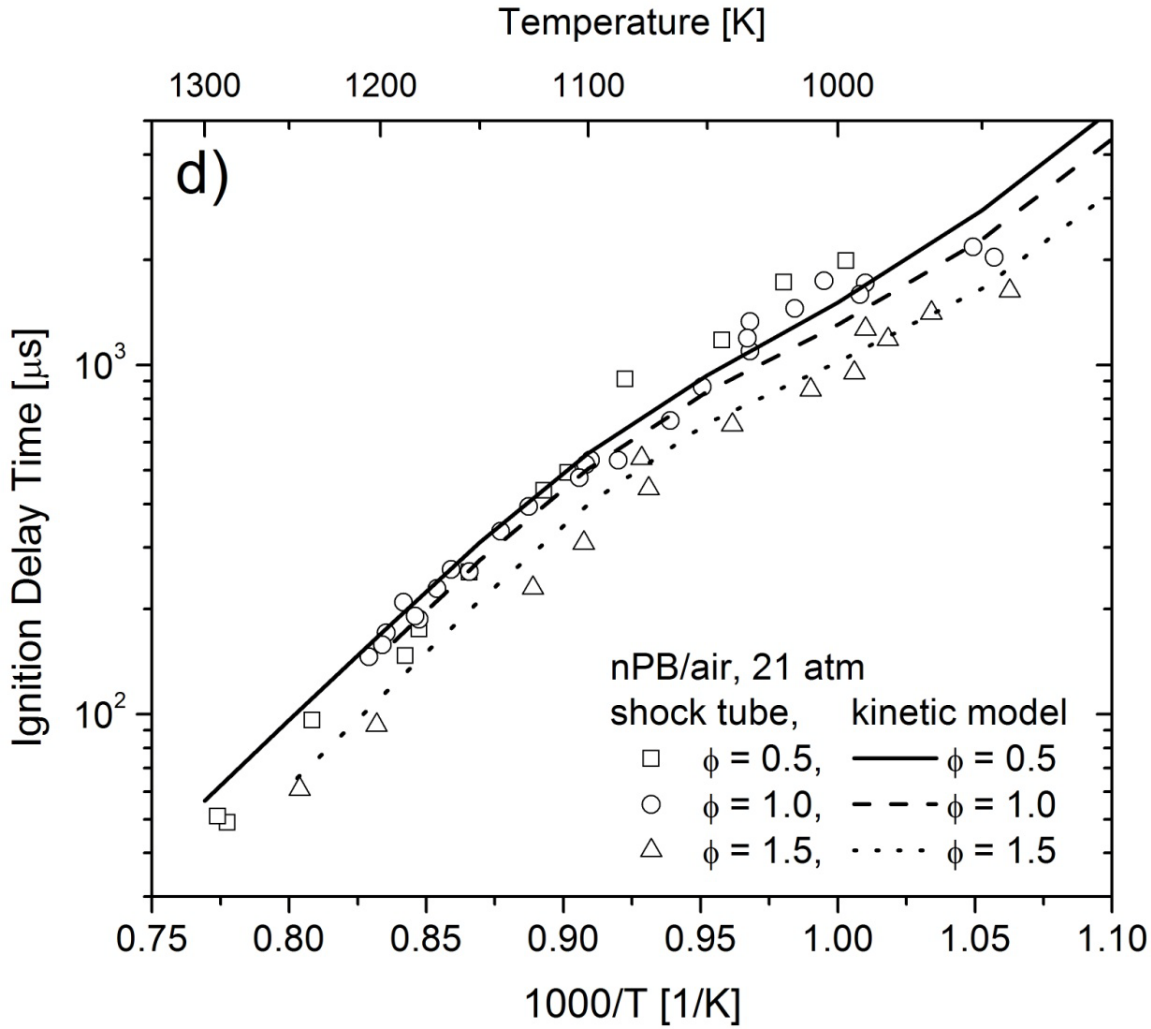
nPB results: variation with P





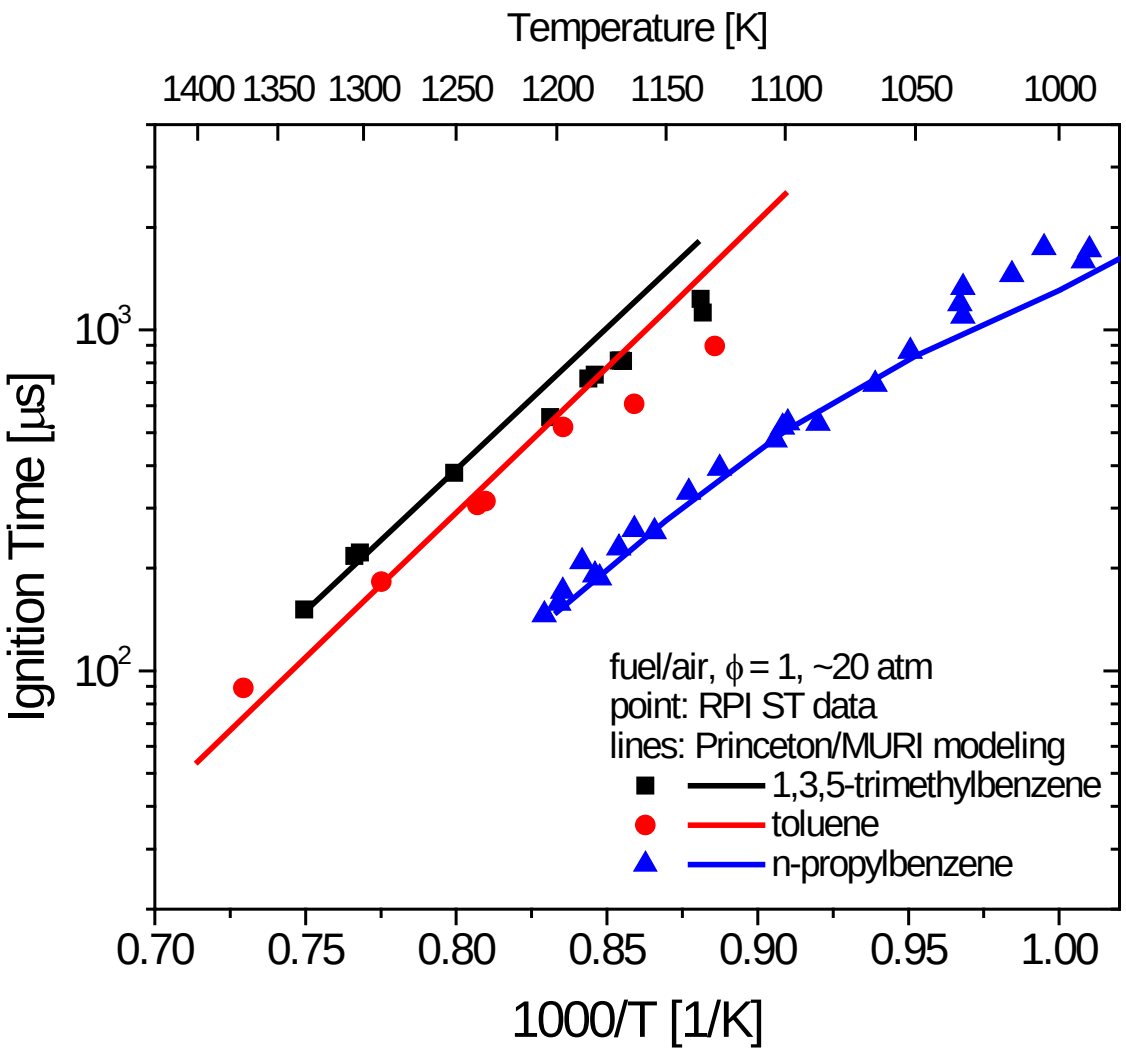
- All experiments for which mild ignition was observed are labeled “perturbed” (crossed-out symbols)
- Kinetic modeling (constant volume) agrees well with data for all experimental conditions not “perturbed”

nPB results: variation with Φ



- Φ dependence is weak, particularly on lean side
- Model captures measured Φ dependence

Other aromatics



- Preliminary first-cut 135-trimethylbenzene modeling appears reasonable
- Comparison of 135-TMB, toluene, and nPB illustrate the influence of the side chains

Summary

- Jet fuel ignition delay times now available for:
  - Jet A (POSF 4658) /air mixtures at ϕ = 0.25-1.5 and 7-39 atm
  - S-8, Shell FT, Sasol IPK at ϕ = 1.0 and 20 atm
  - High-T ignition delays are similar for all jet fuels studied to date over the conditions considered
  - Low-T ignition delays differ depending on composition: branching and aromaticity
- Studies ongoing for branched alkanes and aromatics

Acknowledgements

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