The role of uncertainty quantification within kinetic model improvement in combustion

Alison S. Tomlin

In combustion complex chemical mechanisms built by:

> proposing sets of rules for species interactions:

> **mechanism protocol.**

> developing **effective parameterisations** for the kinetics described within the mechanism.

- Ability to specify protocols well developed e.g. hydrocarbon oxidation.

- Large comprehensive mechanisms e.g. biodiesel surrogate methyl decanoate: 3012 sp., 8820 reacs (Herbinet et al., 2008)

- Many rate coefficients have to initially be estimated using rules related to chemical structure.

- **Does this lead to a robust mechanism? How can the model robustness be improved?**
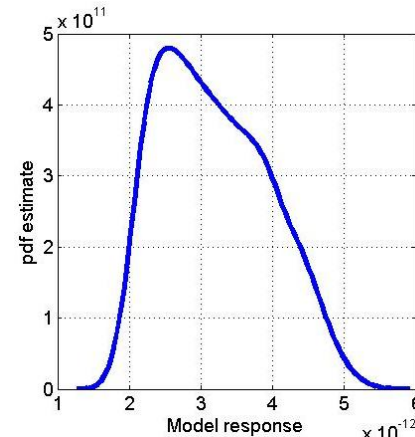
Improving model robustness

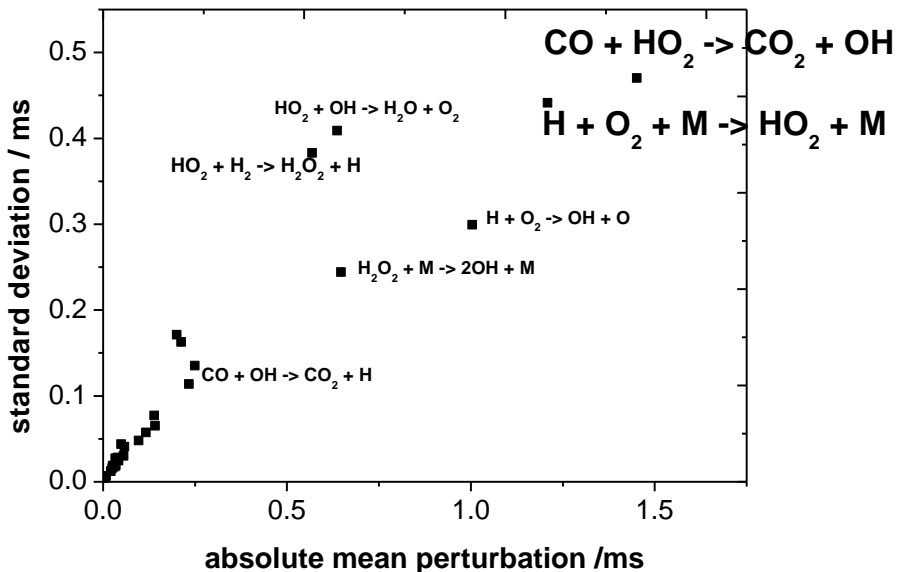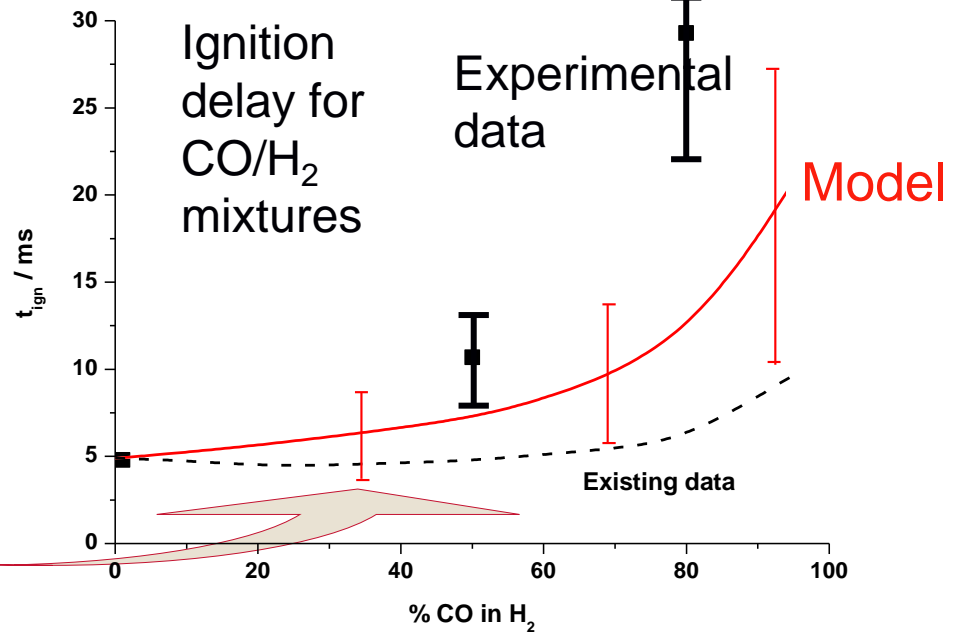**Joint pdf of inputs**
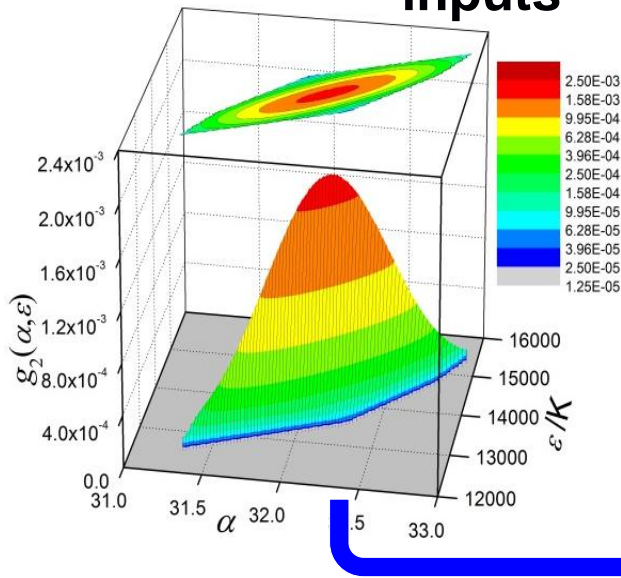
Probability distribution of predicted Y_i

We would like to narrow the output distribution as far as possible i.e. to reduce predictive error bars.

Sensitivity and uncertainty analysis

• **Uncertainty analysis (UA)** puts error bars on predictions.

• Overlap (or not) with experimental values tells us whether our model may be structurally robust.

Sensitivity analysis (SA) tries to determine how much each input parameter contributes to the output uncertainty (usually variance).

Ignition delay for CO/H_2 mixtures

Experimental data

Model

Existing data

t_{ign} / ms

% CO in H_2

standard deviation / ms

absolute mean perturbation /ms

$CO + HO_2 \rightarrow CO_2 + OH$

$HO_2 + OH \rightarrow H_2O + O_2$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + H_2 \rightarrow H_2O_2 + H$

$H + O_2 \rightarrow OH + O$

$H_2O_2 + M \rightarrow 2OH + M$

$CO + OH \rightarrow CO_2 + H$

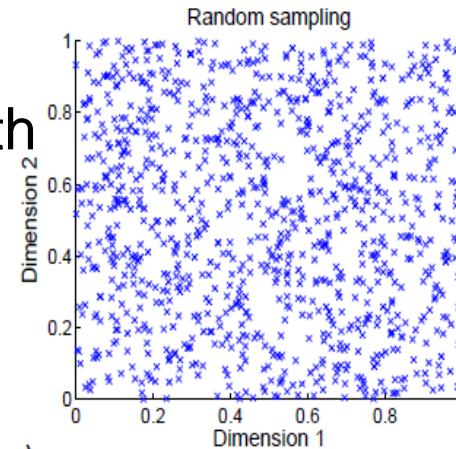Global - attempts to cover whole input space using a sampling method.
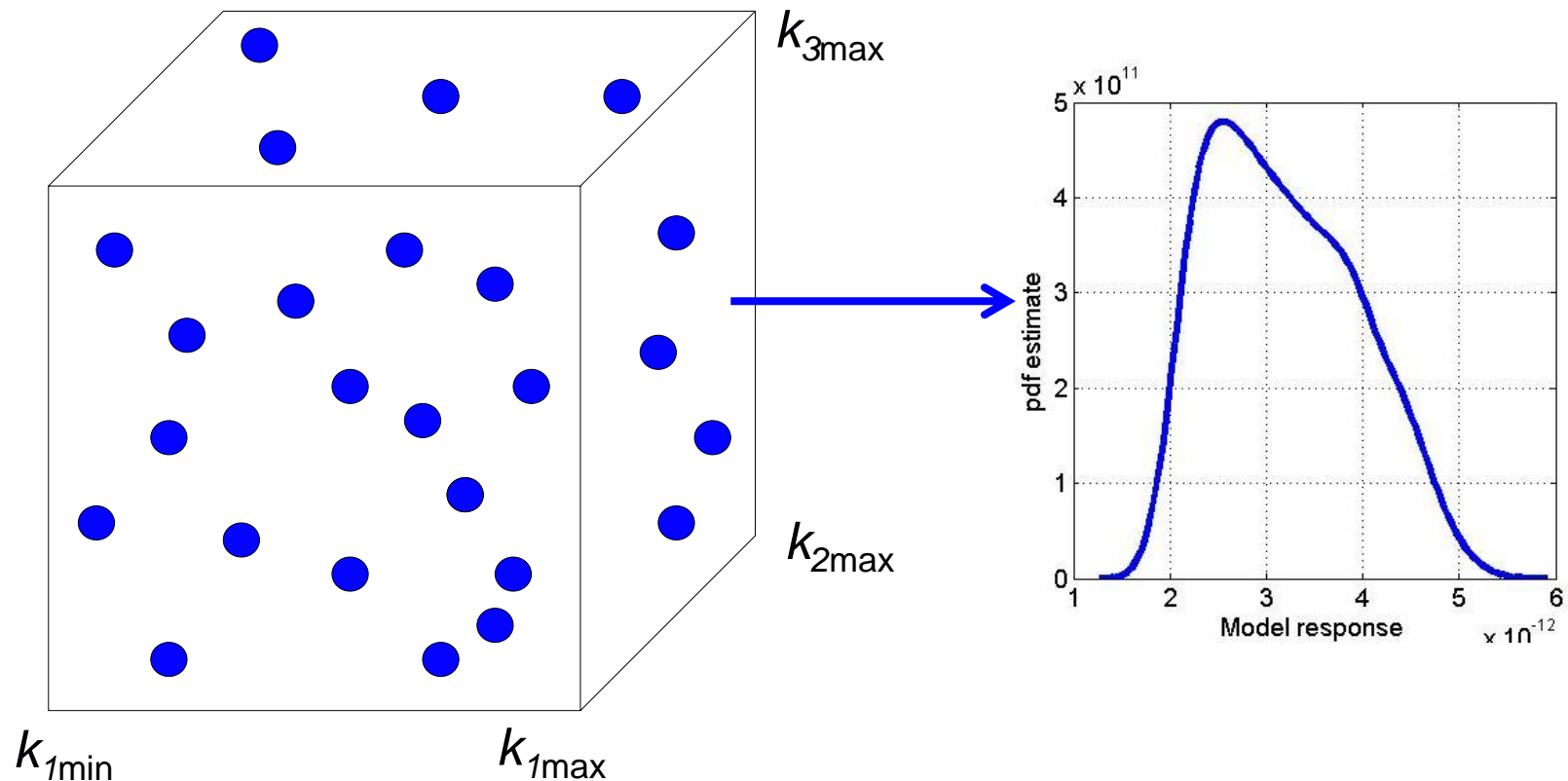
Sampling methods can be computationally costly so why bother.

- To simulate output distributions for available targets.

- To calculate the contribution of important parameters to these distributions however large their uncertainty ranges.

- To see how each target helps to constrain a parameter

  - ➢ Could be important for the use of optimisation approaches where parameter isolation helps to narrow constraints.
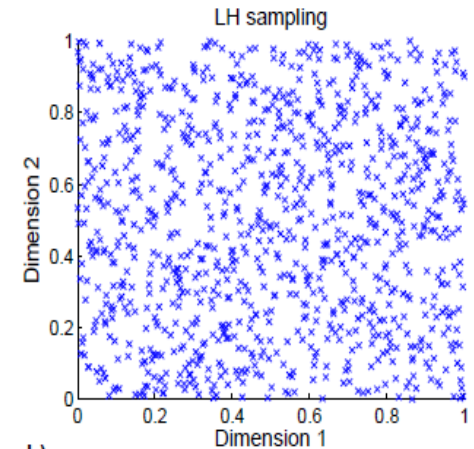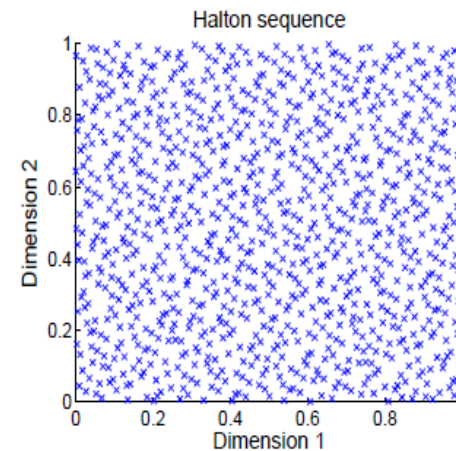
- To explore parameter interactions.

• Need efficient sampling approach where the output moments converge quickly with sample size.

• Quasi-random approaches usually work best.

• Sample from input distributions until predicted output mean and variance converge.

• Then need a method to investigate input-output relationships.
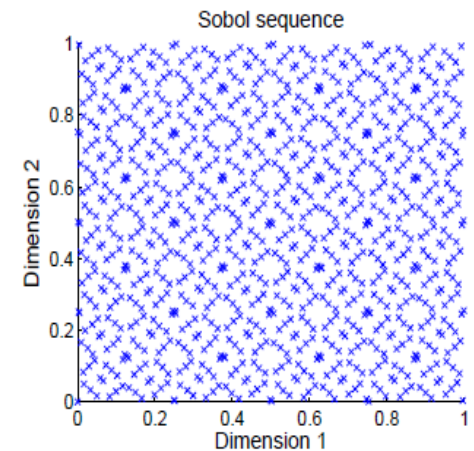
- Input-output relationship is expressed as a finite hierarchical function expansion:

$$f(\mathbf{x}) \equiv f_0 + \sum_{i=1}^{n} f_i(x_i) + \sum_{1 \leq i \leq j \leq n} f_{ij}(x_i, x_j) + \ldots + f_{12\ldots n}(x_1, x_2, \ldots, x_n)$$

- Model replacement built using quasi random sample and approximation of component functions by orthonormal polynomials.

- Equivalent to ANOVA distribution so each term represents contribution to overall output variance.

- 1st & 2nd order sensitivity indices easily calculated from polynomial coefficients.

- Component functions reveal independent mean effect of each parameter and highlight any non-linear responses.

- Local S'_i at the nominal value may be quite different from the overall effect across the feasible parameter range.
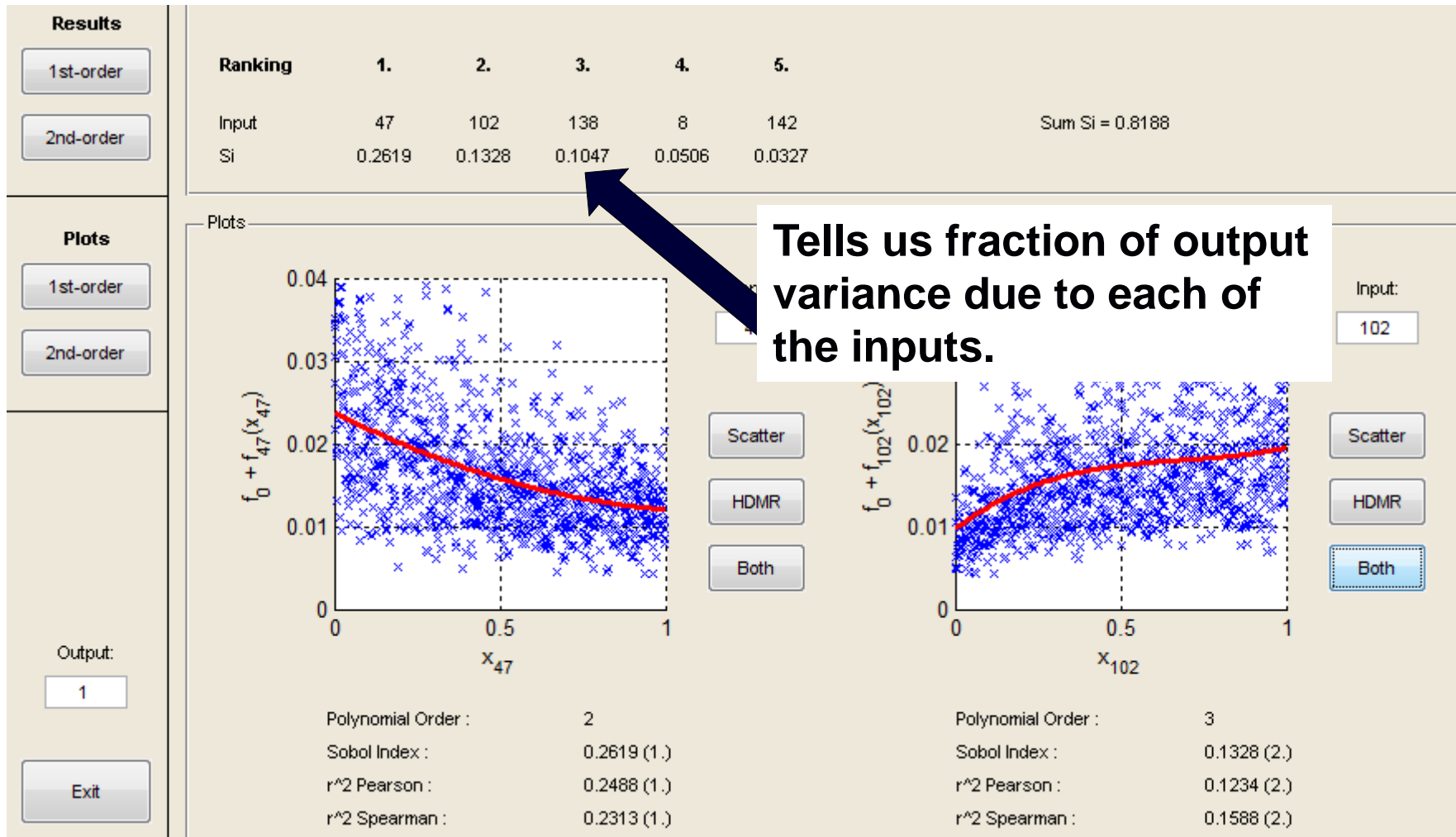
- Scatter reveals influence of other parameters.

a) / b)
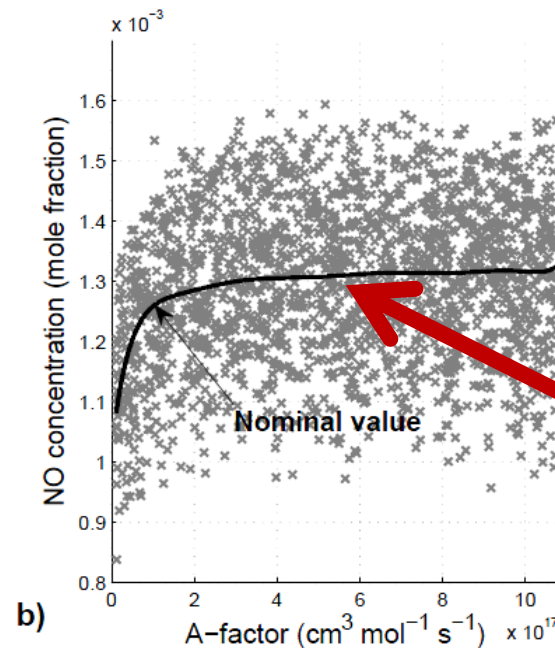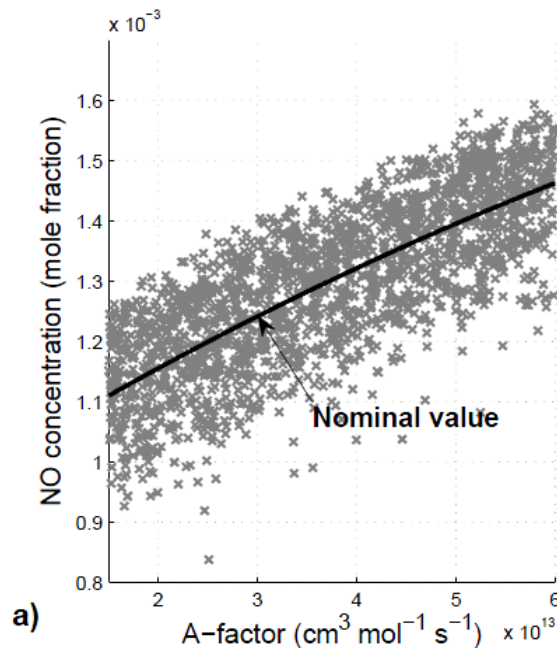
Example from flame calculation: NOx prediction.

Highly nonlinear

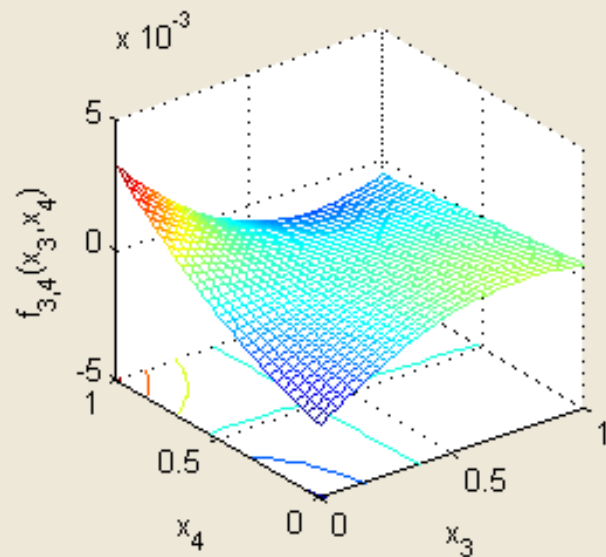# 1st order sensitivities and ranking + component functions

Tells us fraction of output variance due to each of the inputs.

UNIVERSITY OF LEEDS

UNIVERSITY OF LEEDS
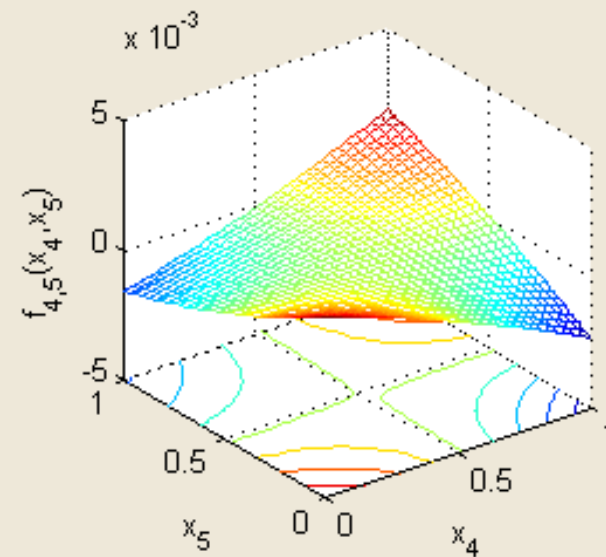
• Constructed mechanism incorporated within model which simulates chosen experimental targets:

➢ flame speeds, ignition delays, JSR concentration profiles

• Agreement with targets assessed and sensitivity analysis performed.
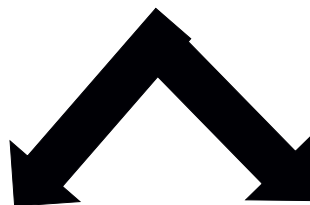
Updates made to key parameters e.g. through theory or direct experiments

Mechanism optimised using available targets from indirect experiments

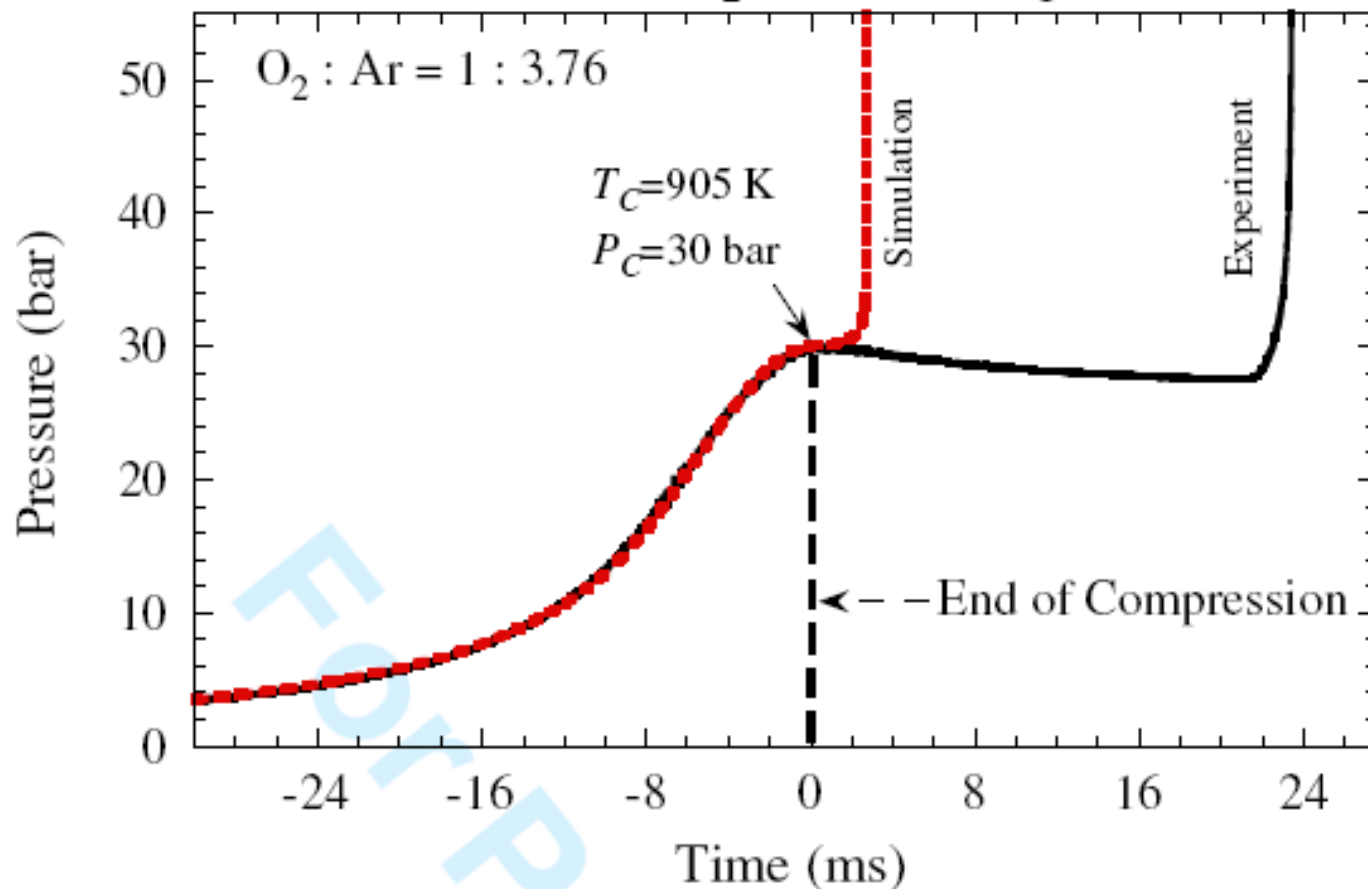# Example 1

Methanol oxidation

(a) Methanol/O_2/Ar, ϕ=1.0, P_C=30 bar

Constraints from the experiments?
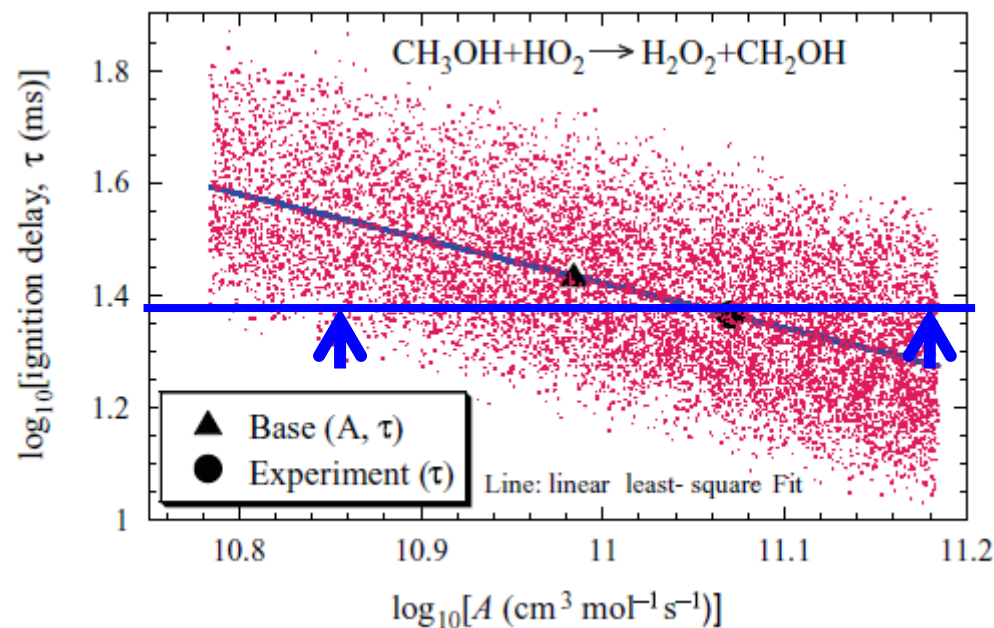
Impact of modifying rate to Tsang value
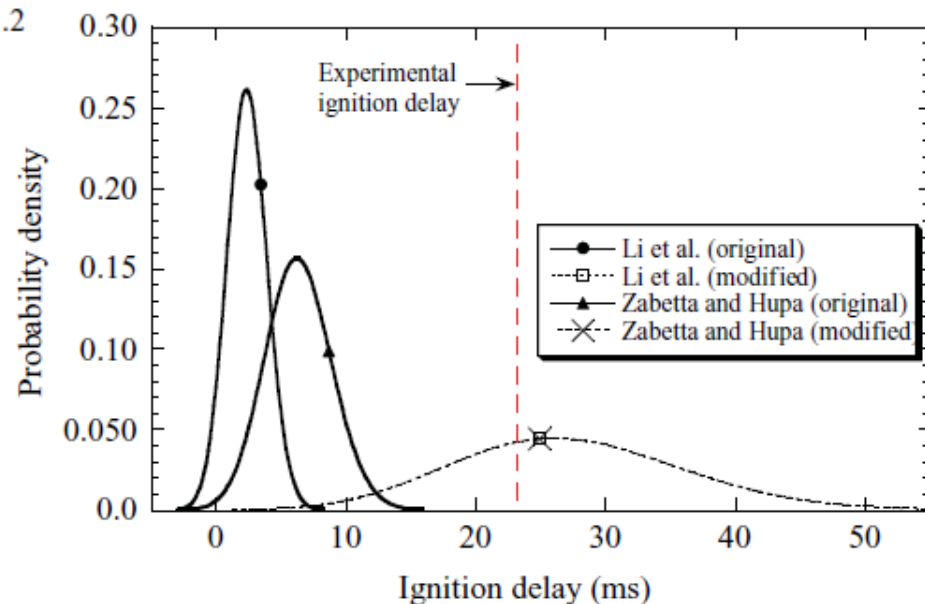
UNIVERSITY OF LEEDS

- Mechanism - Li et al. (2007); 18 species, 93 reactions.

- Target output - ignition delay time (τ) for stoichiometric mixtures of methanol and oxygen over a range of temperatures and pressures.

- Enthalpies of formation and *A*-factors varied over random sample.

- Using initial ranges one reaction dominates (up to 90% of total output variance) with strong **nonlinearities**.
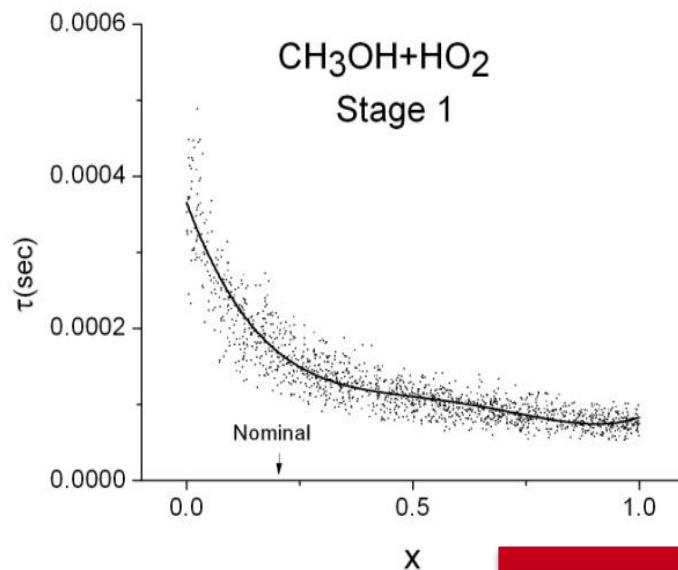
Low scatter indicates low influence of all other parameters.

(T,P,φ)=(1150K,5bar,1)

Sensitivity mapping over *P/T*

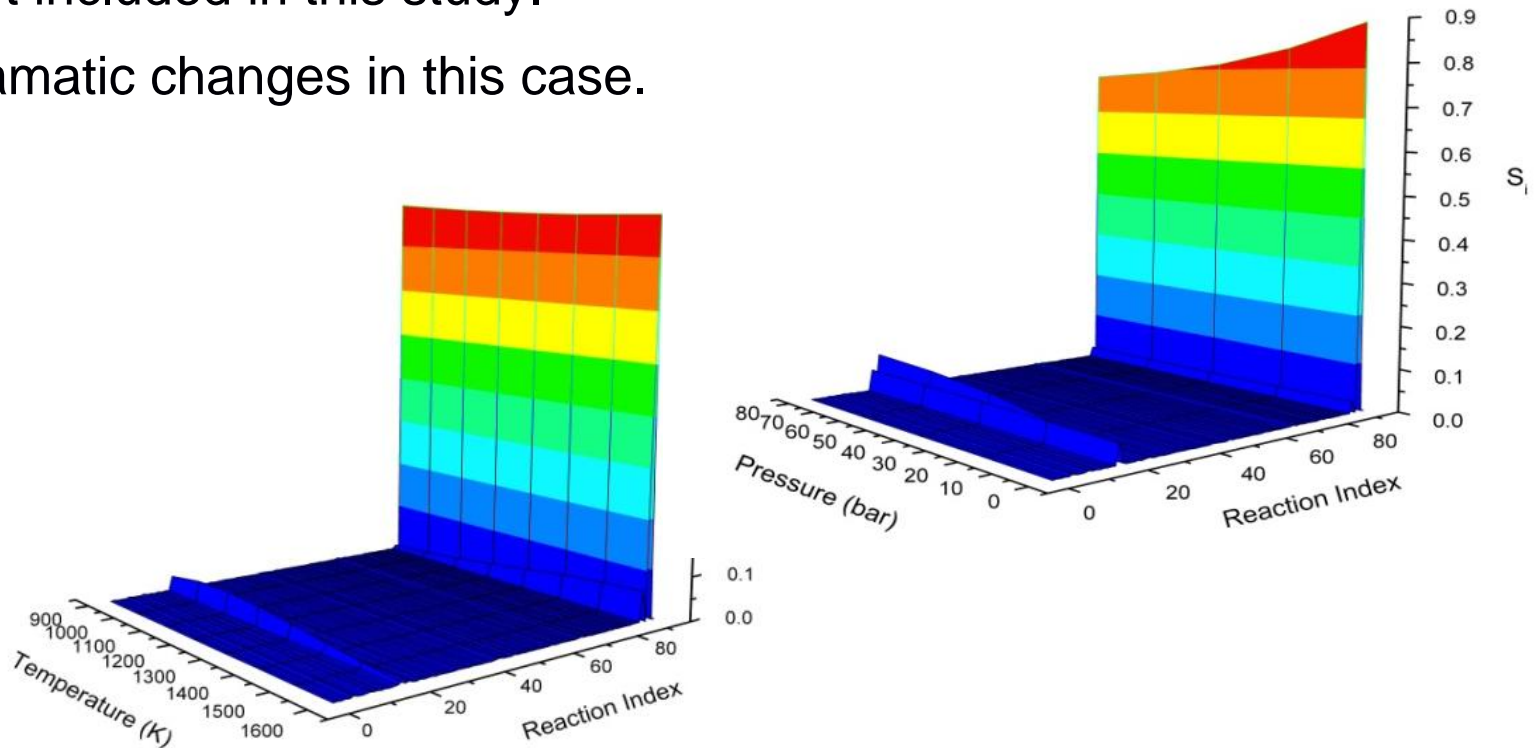• Can also test how sensitivities change outside of conditions where experimental data exists - although uncertainties in activation energies were not included in this study.

• No dramatic changes in this case.

- CH$_3$OH+HO$_2$ a key reaction with initial uncertainty (10^f) of 5.

- Transition state theory (TST) and variational TST (VTST) then used to re-estimate its rate coefficient (Klippenstein,2011).

- Lower than value in Li at low T (**8 times i.e. larger than 5!**) with an **estimated** uncertainty of 2.
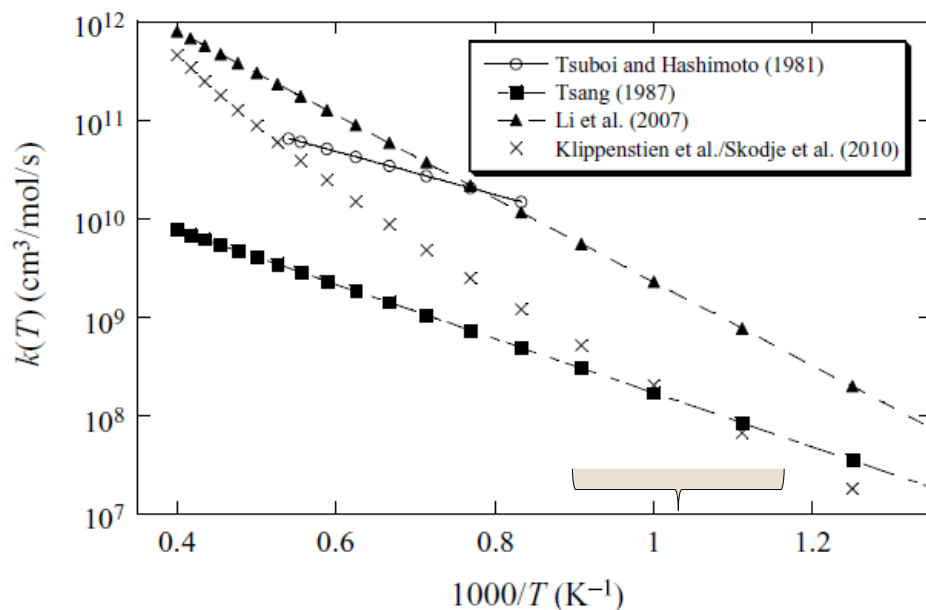
- Close agreement between new value and that of Tsang at low temperatures.

- Closer to Li value at high temperatures.

Stage 1 – Li mech

Stage 2 – CH$_3$OH +HO$_2$ updated TST

Stage 3 - CH$_3$OH +O$_2$ updated TST

$10^f \sim 2$
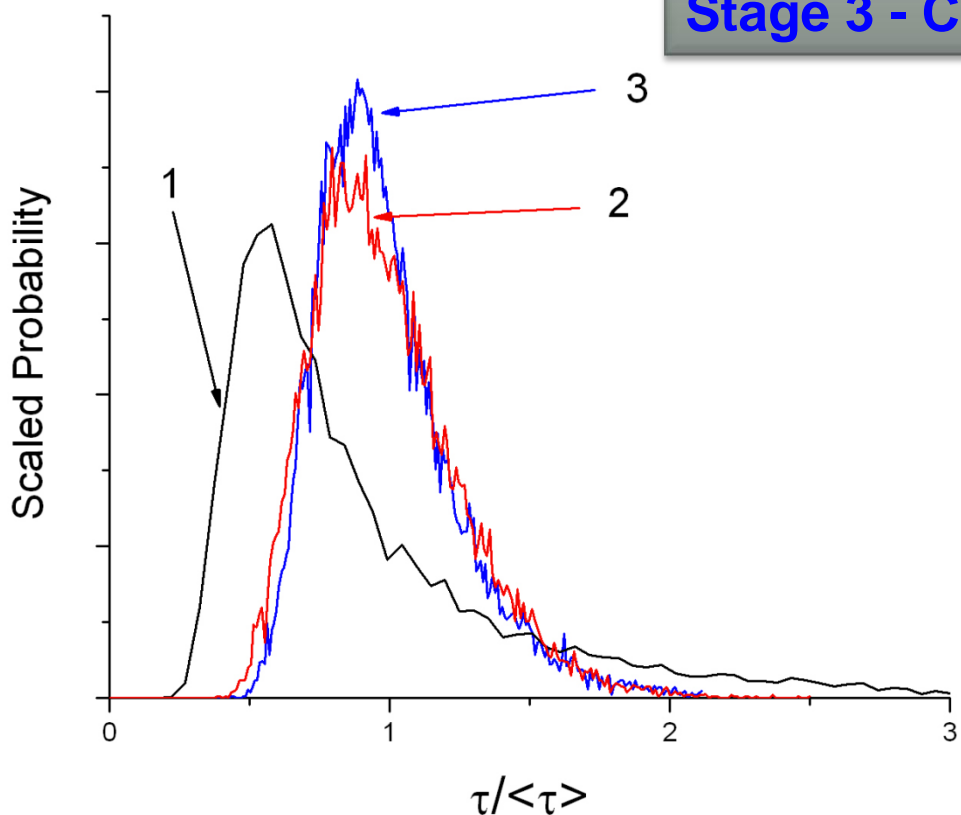
(T,P,φ)=(1150K,5bar,1)

- Modified rates from both studies are similar at low-intermediate temperatures - well constrained?

- Low sensitivity of high T shock tube simulations (Bowman 1975) and predicted flame speeds.

- High sensitivity to flow reactor data at 970 K and 2.5 atm.
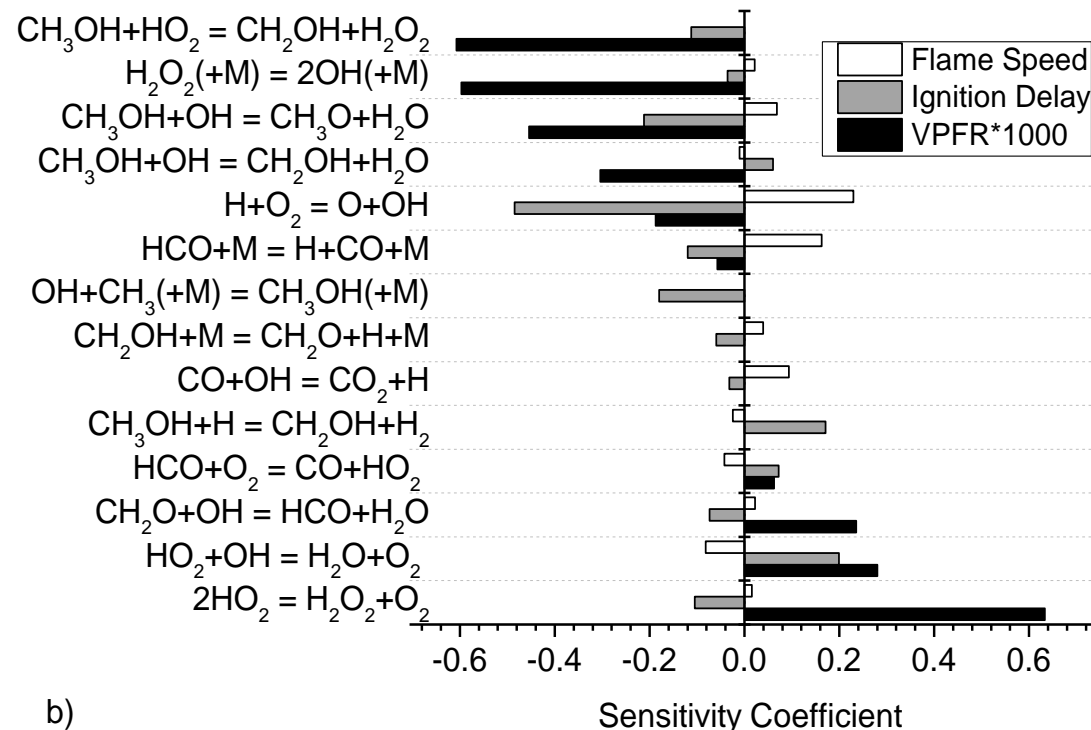
b)

How to combine knowledge?

- The reaction exhibits sensitivities for several reaction systems.

- Should start to become parameter focussed rather than mechanism/target focussed?

- Possibility to incorporate all sets of data to which a parameter is sensitive within a Bayesian framework.

- Does this get too messy for complex fuels?
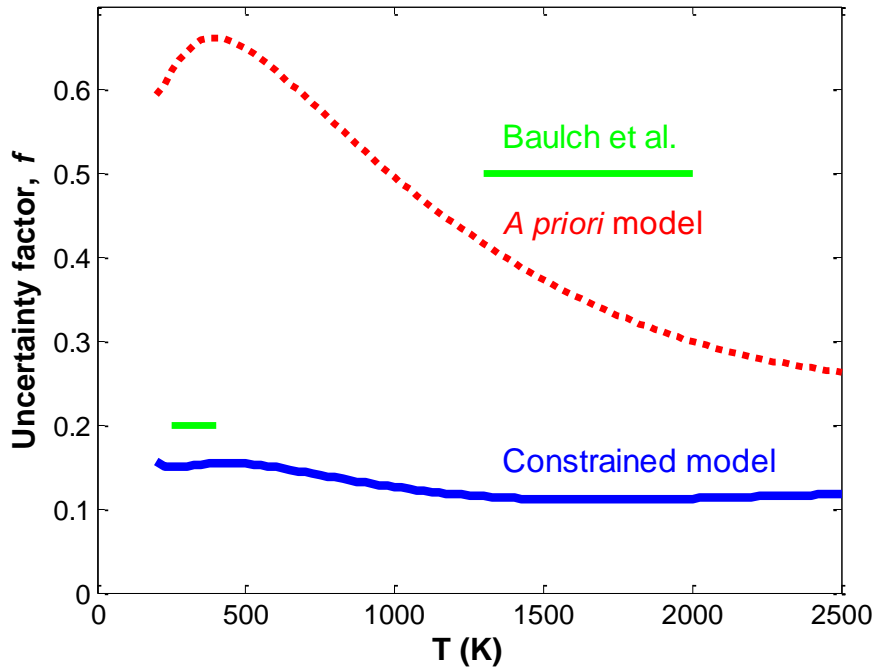
$HO_2+OH=H_2O+O_2$, Burke et al. 2012

Data from TST, discharge flow, shock tubes used.

$H+O_2=OH+O$, Turányi et al. 2012

Data from ignition delays, shock tubes
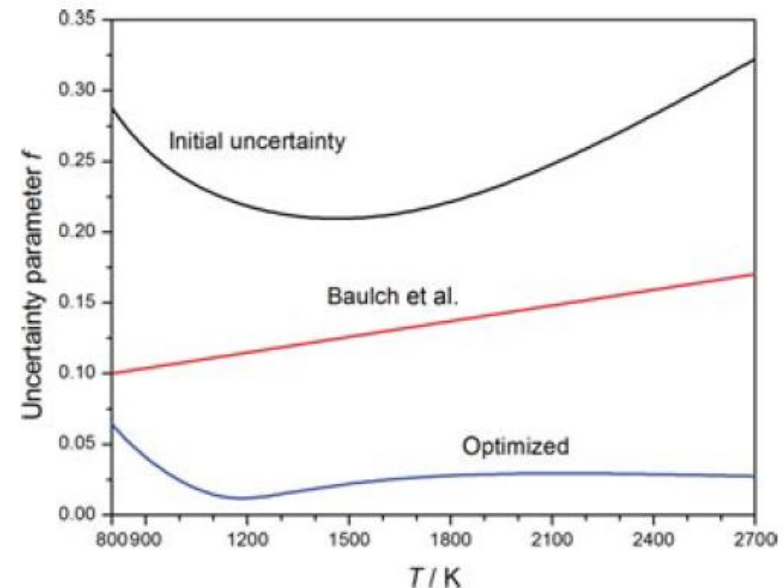
Larger fuels?

- Target predictions for more complex mechanisms are unlikely to be driven by only 1 or 2 parameters.

- What type of approach should be adopted?

- A hierarchical one where the simpler and better constrained systems are tackled first?

  ➢ Turányi's approach only selects data which is strongly sensitive to parameters being constrained i.e. reasonably well isolates parameters.

- The resulting more tightly constrained parameters could then be included in studies of more complex fuels – helping to isolate the other reactions.

Example 2: Butane oxidation in a jet stirred reactor

Performance of EXGAS mech.

Isothermal jet-stirred reactor

1 atmosphere

Residence time : 6 s

Equivalence ratio of 1

4% butane as inlet mole fraction.

Methodology
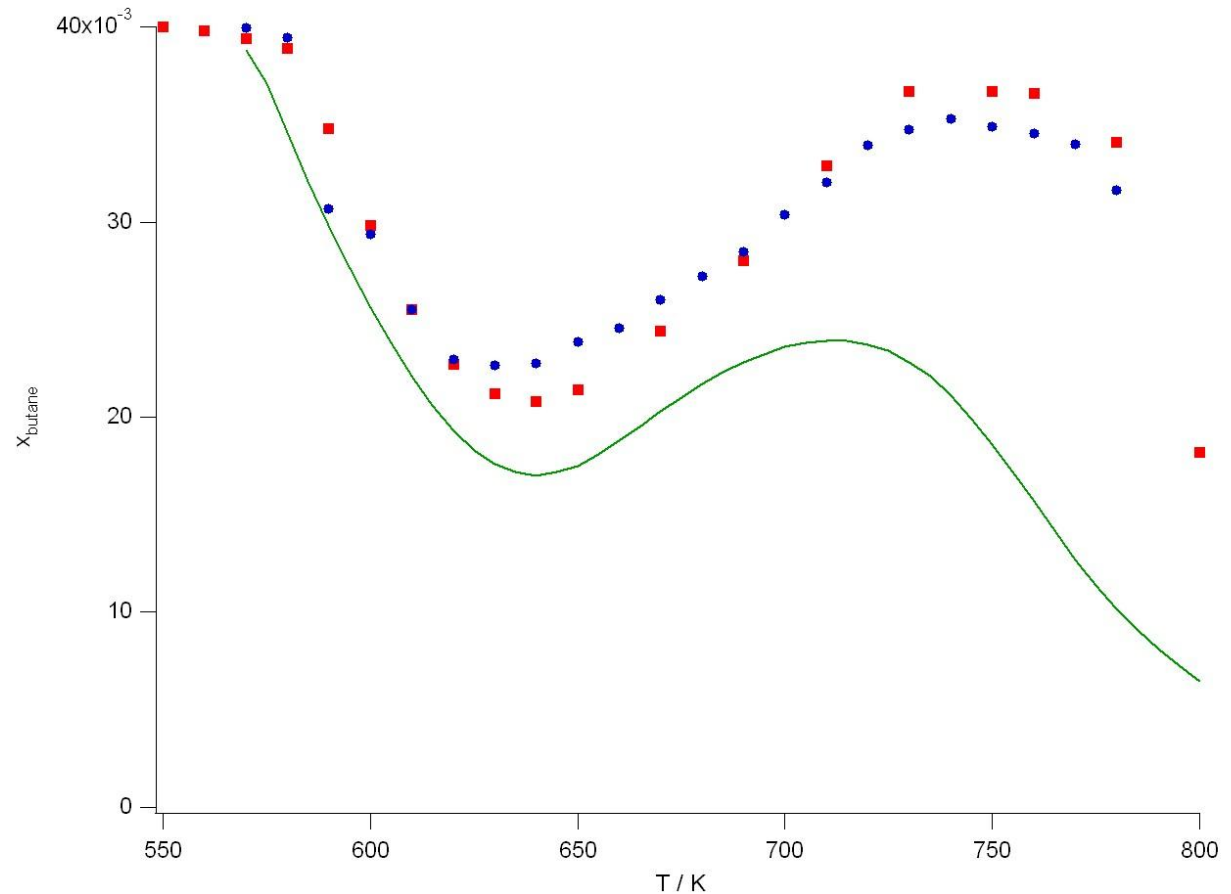
• EXGAS mechanism - 1304 uncertain *A*-factors for forward reactions studied.

• Very large dimensional input parameter space.

• Screen out unimportant parameters before full global analysis.

• Linear sensitivities at several temperatures used for screening.

• Gives better coverage for remaining parameters allowing smaller sample size.

- 31 *A*-factors selected for global runs based on the linear screening.
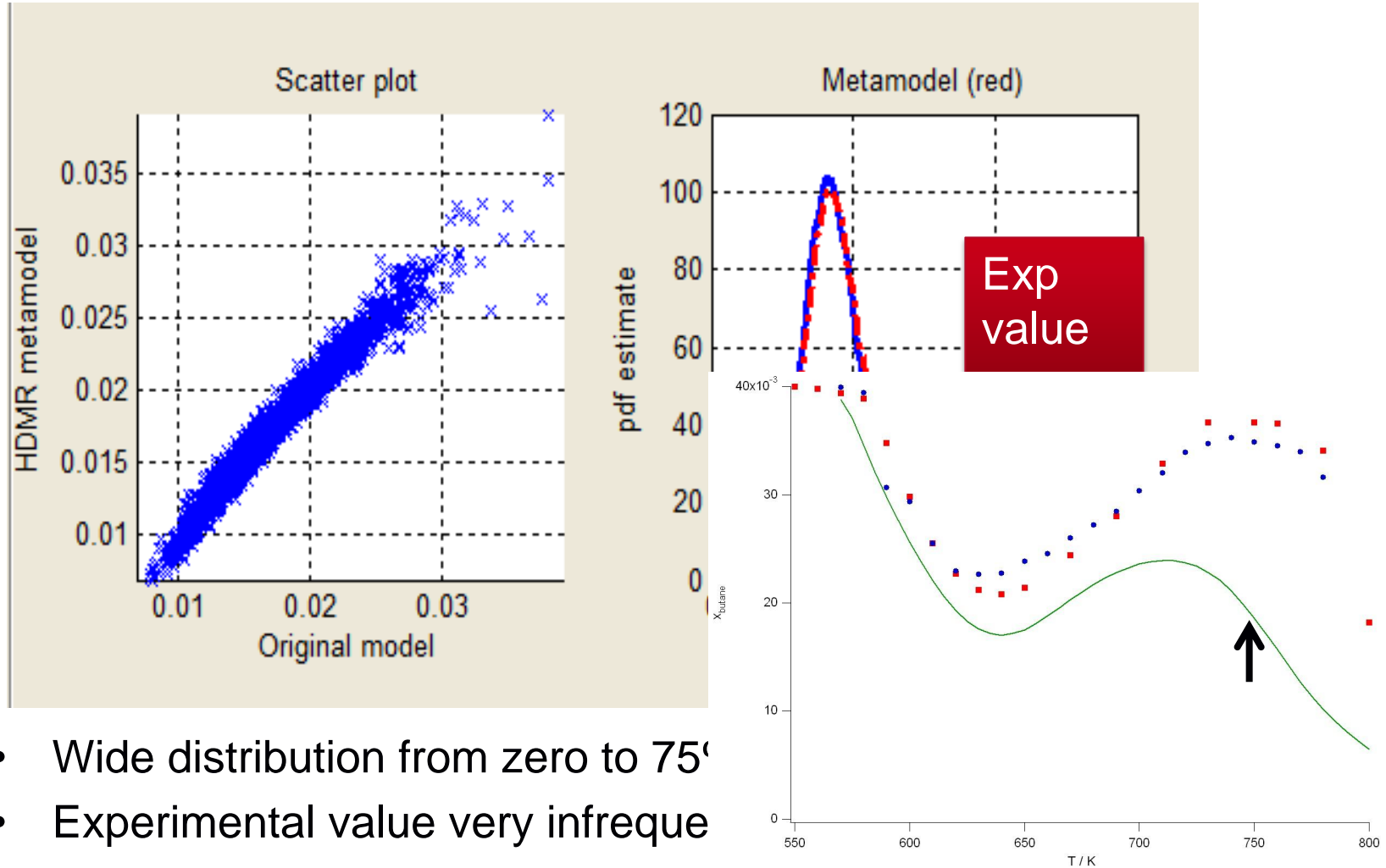
- Input uncertainty factors assigned from appropriate evaluation studies where available - C_0-C_2 reactions base (Baulch *et al.* 1994) .

- For calculated parameters within the primary and secondary mechanisms, $10^f \sim 3$.

- n-butane + OH $10^f \sim 0.3$ used based on (Sivaramakrishnan *et al.* 2009).
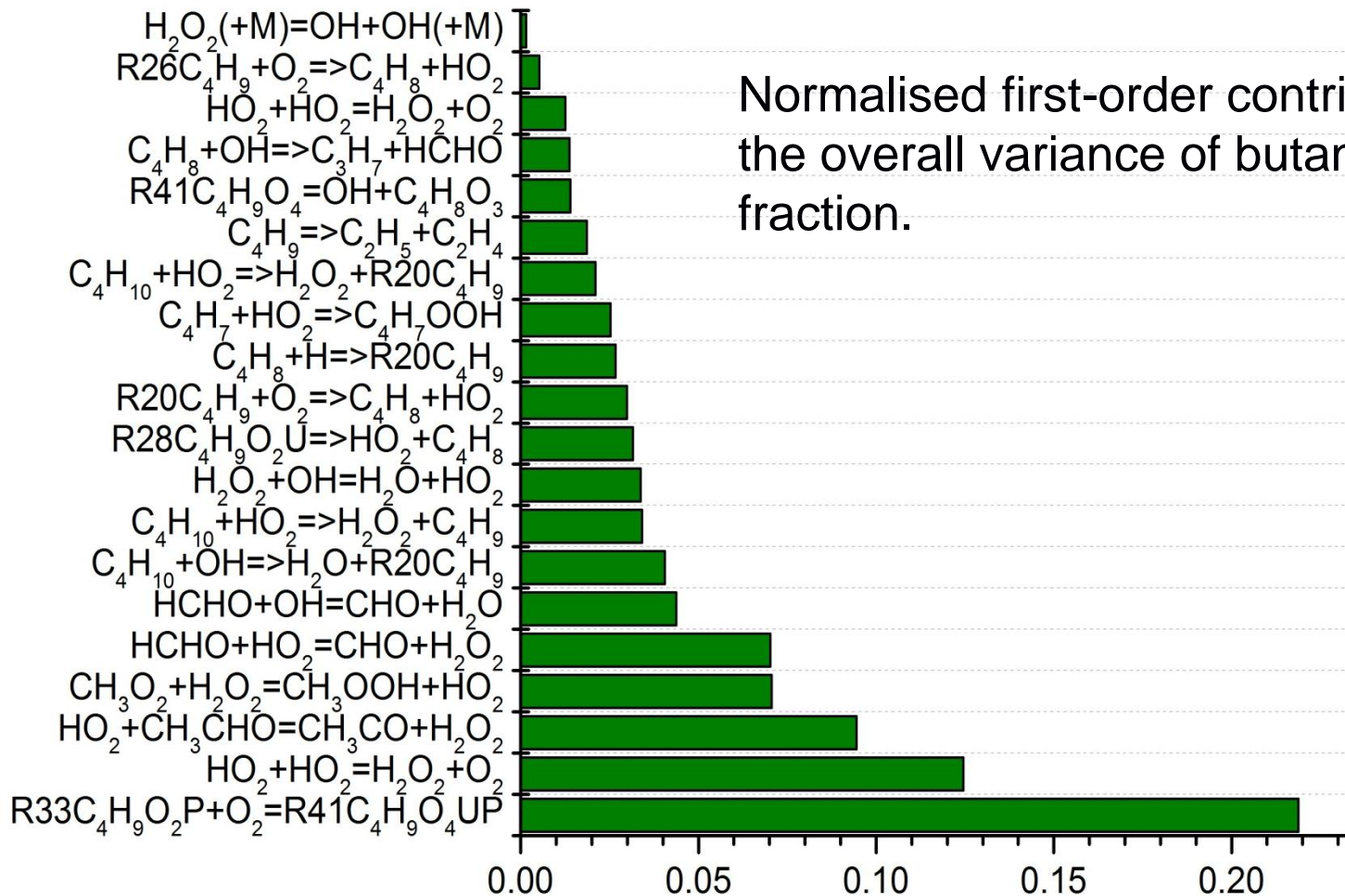
- Wide distribution from zero to 75°
- Experimental value very infreque
- Missing steps or too tight uncertainties used?

JSR (T_{res} 6 s, P 1 atm, stoich, 4% n-butane, 750 K)

Normalised first-order contributions to the overall variance of butane mole fraction.

Improving model robustness?

- The ntc region appears to be highly uncertain.

- Many reactions contribute to uncertainty.

- Are there missing steps or are assumptions about input uncertainties optimistic?

- Should a hierarchical Bayesian approach be adopted?

  ➤   Start first with H_2/O_2 chemistry.

  ➤   Then tackle HCHO reactions.

  ➤   Then C2 chemistry.

  ➤   Then try to constrain reactions from C4 scheme.

- What other experiments could help to constrain these important parameters and how do we find out?

HO$_2$+HO$_2$ (Zhou et al. 2012)
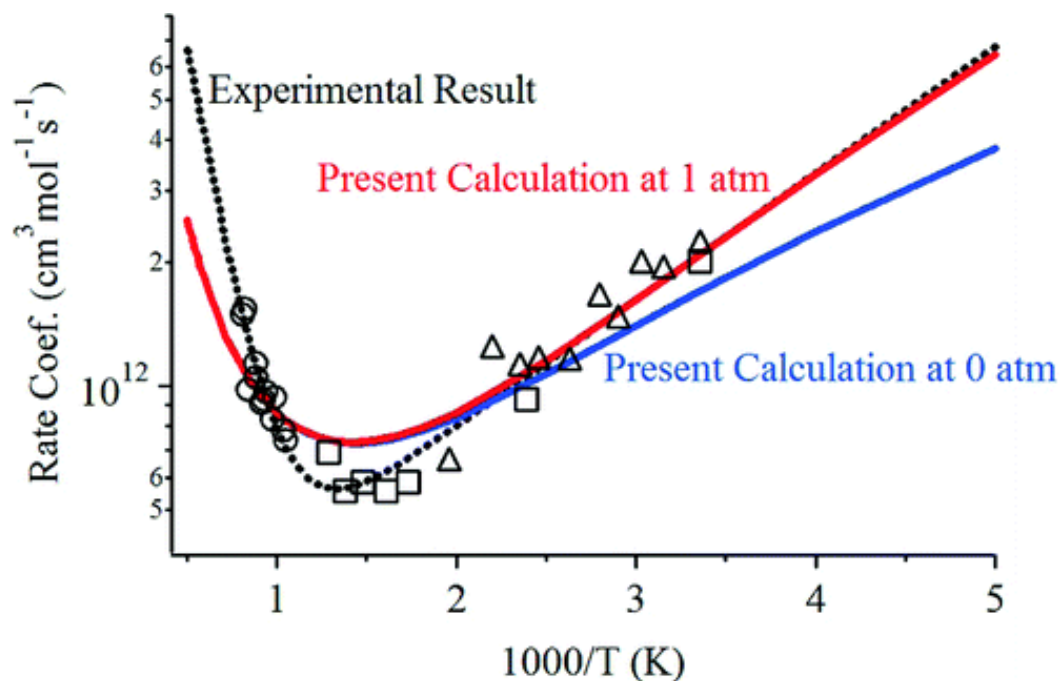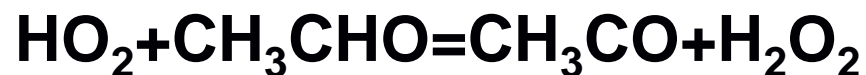
- TST calculations.
- Transition state ridge upward by 1 kcal/mol to better fit experiments of Patrick, Lightfoot and Kappel.

- Original f_{max} (Baulch 1994) was 0.4.

- Probably could be reduced using optimisation approaches.

Aldheydes + HO$_2$

HO$_2$+CH$_3$CHO=CH$_3$CO+H$_2$O$_2$
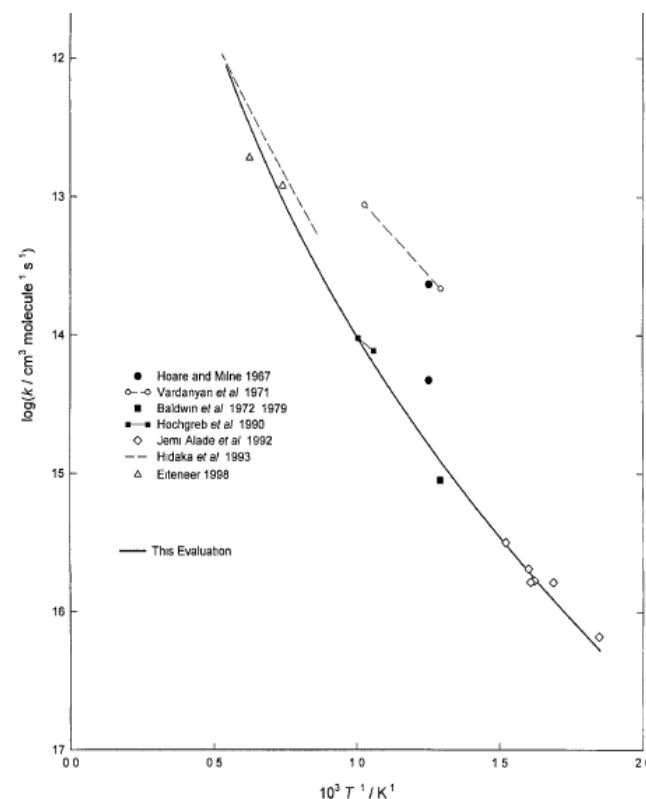
- Baulch (2005) suggests f_{max} of 0.7.

- Based on a single set of experimental measurements from 1976 (Colket et al.).

HO$_2$+HCHO=CHO+H$_2$O$_2$

- Baulch (2005) suggests f_{max} of 0.4.

- Recent TST calcs. from Li *et al. 2005*

- Combined analysis?

What new sets of data could help to constrain these parameters better?

exp

A-factor for reaction
R33C$_4$H$_9$O$_2$P+O$_2$=R41C$_4$H$_9$O$_4$UP
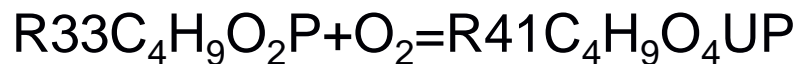
- Very scattered response but data hints that rate is might be lower than the nominal value used which was based on analogy to rate coefficients for propyl + O$_2$ from De Sain et al. (2003)

- Clearly a key reaction class driving fuel reactivity.

- QOOH+O$_2$ studied for propane and pentane theoretically by Bozzelli and Coworkers but not for butane.

2nd oxygen addition reactions to form O2QOOH

- Rate used was estimated on the basis of analogy to rate coefficients for propyl + O_2 from De Sain et al. (2003)

- Recent theoretical calculations exist from Goldsmith et al. (2012) for the propyl + O_2 system suggest that for the main channel the reaction forming O2QOOH is slower than the equivalent rate for propyl + O_2 at 750 K.

- An equivalent temperature dependant study for butyl would be very useful.

- Still large uncertainties for these types of reactions.

- If basic C1/H scheme was better constrained then then indirect experiments might help to constrain rates for reactions which are difficult to study experimentally.

- Could be useful to collate information about conditions over which certain reactions have high sensitivity coefficients.

    i.e. parameter focus rather than experimental.

- Would involve simulating a lot of data sets over different temperatures and pressures for a lot of different fuels in a consistent way.

- Optimisation approaches which combine data sets are clearly a way forward in terms of reducing input uncertainty distributions.

- Possible for H_2/O_2 chemistry (last talk).

- How to do it for complex fuels raises all sorts of questions.