Appendix A: Delay time distributions

We consider a container filled with gaseous propane C_3H_8 in a closed room of constant volume initially at atmospheric pressure. We assume that the room is adiabatic, which means that all heat losses can be neglected.
Through a leak, a stoichiometric mixture of air-propane is formed in the room. Because of some incident, the ambient temperature jumps from 293.15 K (20 °C) to an initial temperature T_0 following a normal distribution: $T_0 \sim N(\mu_{T_0} = 524\ K, \sigma_{T_0} = 20\ K)$. We have $p(T_0 < 440K) <$ 1E-04 and $p(T_0 > 600K) <$ 1E-04. As a consequence, we can always consider that the initial temperature belongs to the interval $[T_{0,min} = 440$ K$; T_{0,max} = 600$ K$]$ in order to develop an approximation for the critical time.

We decided to describe the system through the theory of thermal explosion of Semenov [1]. According to it, the reaction progress leads to an increase in temperature which itself spawns an increase in the reaction rate that causes the temperature to rise ever faster (*thermal runaway*). Following this theory, the system can be described by the following equations:
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$, $\rho c_v \frac{\partial T}{\partial t} = (-\Delta u_m) r$ and
$r = -\frac{d[C_3H_8]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = Ae^{-\frac{Ea}{RT}}[C_3H_8]^a[O_2]^b$.
$[C_3H_8]$ and $[O_2]$ (mol/cm^3) are the concentrations of propane and oxygen, respectively, ρ (kg/cm^3) is the volumetric mass of the gaseous mixture, c_ν (kcal/(kg·K)) is its thermal capacity at constant volume, *T* (K) is the temperature, *t* (s) is the time, Δu_m (kcal/mol) is the molar reaction energy, *r* (mol/cm^3/s) is the reaction rate, *A* is the pre-exponential factor, *Ea* (kcal/mol) is the activation energy, *R* = 1.987E-03 kcal/(K mol) is the ideal gas constant, and *a* and *b* are reactant coefficients.

According to Westbrook and Dryer [2], the following parameter values can be employed:

Parameter	A_0 (mol, cm,s)	Ea_0 (kcal/mol)	*a*	*b*
Values	8.6E+11	30.0	0.1	1.65

They used laminar flame speeds at atmospheric pressures to calibrate them.

Further in the study, we shall assume that the parameters are uncertain and that $A \in [6.0\text{E+11} ; 8.0\text{E+13}]$ (mol, cm,s) and $Ea \in [27; 46]$ kcal/mol, for example because of analogies with other global reactions. We consider a stoichiometric mixture at atmospheric pressure (*p* = 1 atm = 101325 Pa), which means we have the following mole fractions:
$X_{C_3H_8} = \frac{[C_3H_8]}{[All\ species]} \approx$ 0.0406, $X_{O_2} \approx 0.2029$, $X_{N_2} \approx$ 0.7565.

We are interested in how quickly the mixture reaches the critical temperature[1] *Tc* = 766 K beyond which it would be impossible for someone to intervene to stop the explosion [3]. Let *tc* be the critical delay time defined as $T(tc) = T_c$.
$tc = tc_{A,Ea}(T_0)$ is a function of the kinetic parameters *A* and *Ea* and of the initial temperature T_0. For several values of the kinetic parameters *A* and *Ea*, we computed $tc_{A,Ea}(T_{0,min})$, $tc_{A,Ea}(T_{0,max})$ and $tc_{A,Ea}(T_{0,rand})$ for 40 random values of the initial temperature $T_{0,rand}$ uniformly chosen in the interval $[T_{0,min}; T_{0,max}]$ with the chemical kinetic software **Cantera [4]**. The results are shown in Figure 1.

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[1] also called ignition temperature in a technical context.

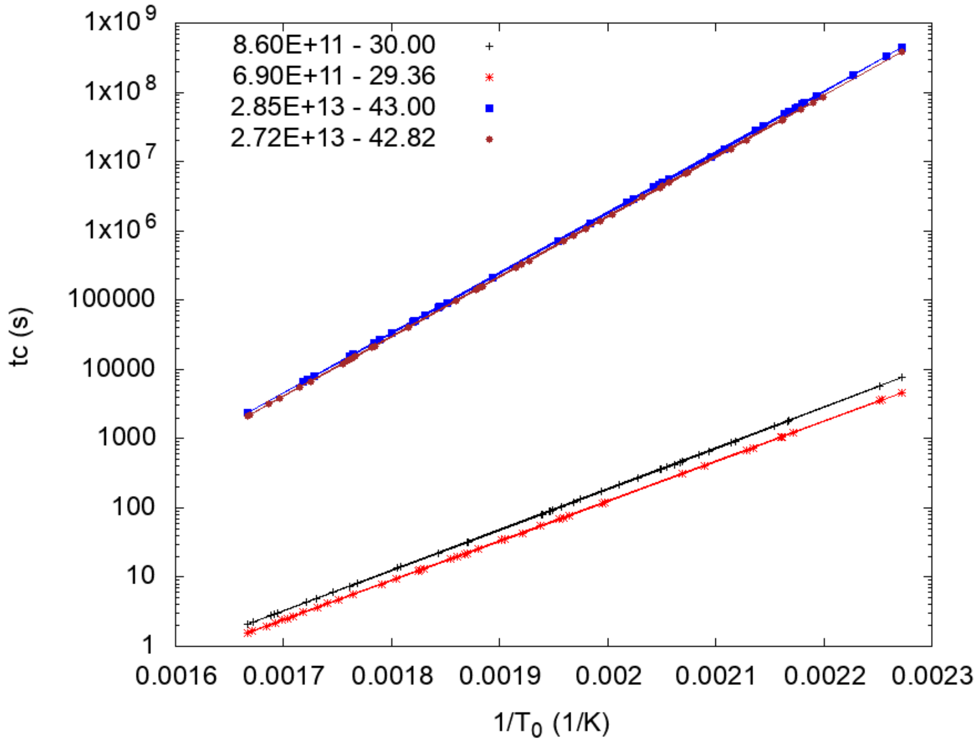


Figure 1: tc as a function of (1/T0) for different (A, Ea) shown in the legend.

We can see that the logarithmic values of the delay time can be well approximated by a linear function of *1/T₀*:

$log10(tc_{A,Ea}(T_0)) = a_{A,Ea}\frac{1}{T_0} + b_{A,Ea}$ with the coefficients

$a_{A,Ea} = \frac{log10\left(tc_{A,Ea}(T_{0,min})\right) - log10\left(tc_{A,Ea}(T_{0,max})\right)}{1/T_{0,min} - 1/T_{0,max}}$ and

$b_{A,Ea} = log10\left(tc_{A,Ea}(T_{0,min})\right) - a_{A,Ea}\frac{1}{T_{0,min}}$.

$log10\left(tc_{A,Ea}(T_{0,min})\right)$ and $log10\left(tc_{A,Ea}(T_{0,max})\right)$ also turn out to be well approximated by a bilinear function of *log10(A)* and *Ea*, as can be seen in Figure 2 and 3. They were obtained with a regular grid containing 30*30 values of (A, Ea). We used the results to create a **piece-wise** bilinear interpolation model of $log10\left(tc_{A,Ea}(T_{0,min})\right)$ and of $log10\left(tc_{A,Ea}(T_{0,max})\right)$ as a function of *A* and *Ea*.

Let us suppose we want to approximate $log10\left(tc_{A,Ea}(T_0)\right)$ for arbitrary values of *A*, *Ea* and T_0 belonging to the intervals defined above.
We start by predicting $log10\left(tc_{A,Ea}(T_{0,min})\right)$ and $log10\left(tc_{A,Ea}(T_{0,max})\right)$ with the piece-wise bilinear interpolation model.

We then compute the coefficients $a_{A,Ea} = \frac{log10\left(tc_{A,Ea}(T_{0,min})\right) - log10\left(tc_{A,Ea}(T_{0,max})\right)}{1/T_{0,min} - 1/T_{0,max}}$ and $b_{A,Ea} = log10\left(tc_{A,Ea}(T_{0,min})\right) - a_{A,Ea}\frac{1}{T_{0,min}}$.

We finally have: $log10\left(tc_{A,Ea}(T_0)\right) \approx a_{A,Ea}\frac{1}{T_0} + b_{A,Ea}$.

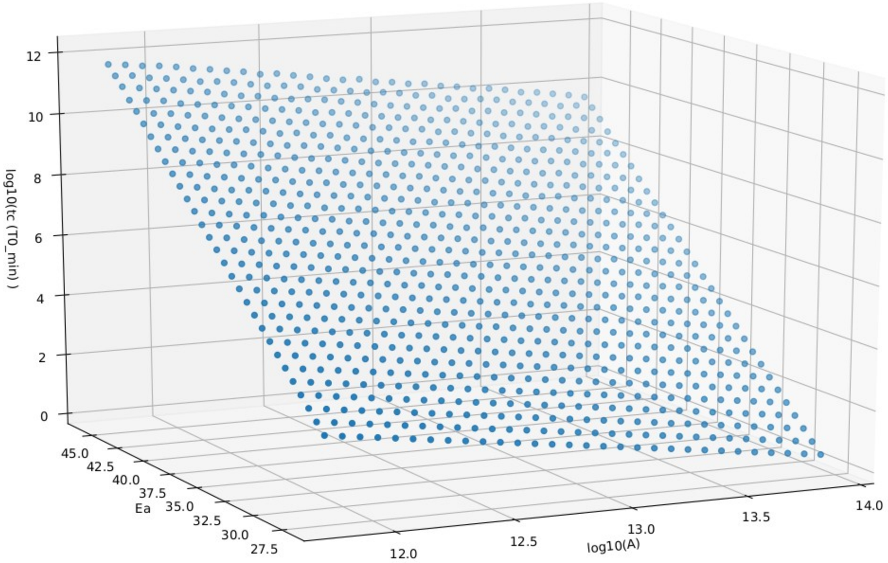


Figure 2: $log10\left(tc(T_{0,min})\right)$ *as a function of (A, Ea)*

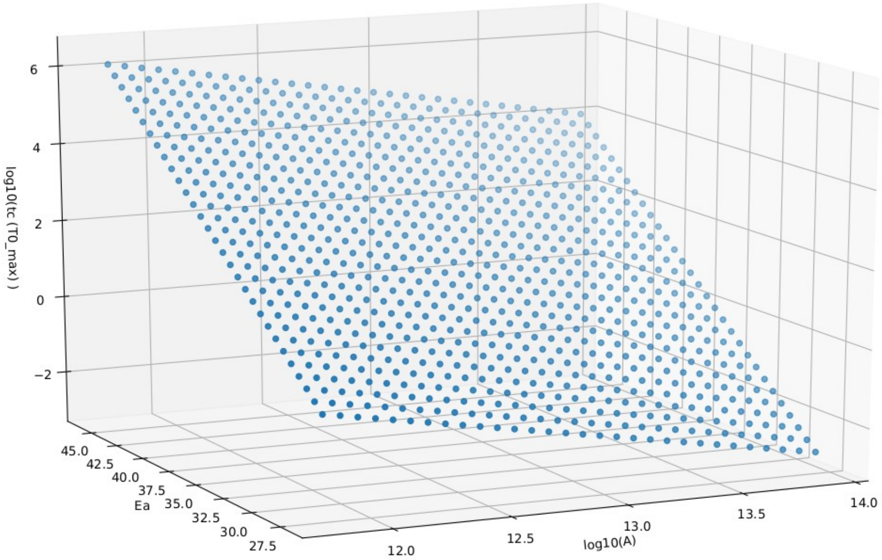


Figure 3: $log10\left(tc(T_{0,max})\right)$ *as a function of (A, Ea)*

The quality of the model has been tested by generating 3000 random values of (*A*, *Ea*) and T_0 with $A \sim U(A_{min}, A_{max})$, $Ea \sim U(Ea_{min}, Ea_{max})$ and $T_0 \sim N(\mu_{T_0}, \sigma_{T_0})$ whereby *U* designates a uniform probability distribution.

We systematically computed $tc_{A,Ea}(T_0)$ with Cantera and $tc_{pred,A,Ea}(T_0)$ with the two linear interpolation models and the relative difference $r = \frac{tc_{A,Ea}(T_0)-tc_{pred,A,Ea}(T_0)}{min\left(tc_{A,Ea}(T_0),tc_{pred,A,Ea}(T_0)\right)}$.

For more than 99.3% of the points, we have $|r| \leq$ 5%.

We have *max(r)* = 12.32% which is reached for a very high delay time superior to 2E+08 s that would be completely unproblematic. Given the fact that we are not interested in numerical accuracy but in understanding the behaviour of probabilistic approaches to thermal runaway hazard, we deemed that level of error to be acceptable.

We now want to compute the probability density distribution of *tc* for the true parameter values A_0 = 8.60E+11 and Ea_0 = 30.

We first compute the coefficients $a_{A_0,Ea_0} = \frac{log10\left(tc_{A_0,Ea_0}(T_{0,min})\right)-log10\left(tc_{A_0,Ea_0}(T_{0,max})\right)}{1/T_{0,min}-1/T_{0,max}}$ and

$b_{A_0,Ea_0} = log10(tc_{A_0,Ea_0}(T_{0,min})) - a_{A_0,Ea_0}\frac{1}{T_{0,min}}$.

We then have $log10(tc_{A_0,Ea_0}(T_0)) = a_{A_0,Ea_0}\frac{1}{T_0} + b_{A_0,Ea_0}$ with $T_0 \sim N(\mu_{T_0} = 525K, \sigma_{T_0} = 20K)$.

The cumulative probability distribution of t_c is given by

$$F(t) = p(tc \leq t) = p\left(log10(tc) \leq log10(t)\right) = p\left(a_{A_0,Ea_0}\frac{1}{T_0} + b_{A_0,Ea_0} \leq log10(t)\right)$$

$$F(t) = p(tc \leq t) = p\left(\frac{1}{T_0} \leq \frac{log10(t) - b_{A_0,Ea_0}}{a_{A_0,Ea_0}}\right) = p\left(T_0 \geq \frac{a_{A_0,Ea_0}}{log10(t) - b_{A_0,Ea_0}}\right)$$

$$F(t) = p(tc \leq t) = 1 - p\left(T_0 \leq \frac{a_{A_0,Ea_0}}{log10(t) - b_{A_0,Ea_0}}\right) = 1 - \Phi\left(\frac{a_{A_0,Ea_0}}{log10(t) - b_{A_0,Ea_0}}, \mu_{T_0}, \sigma_{T_0}\right)$$

where $\Phi(x, \mu_{T_0}, \sigma_{T_0})$ is the cumulative probability distribution of the normal distribution.

Hence $f(t) = F'(t) = \left(-\Phi\left(\frac{a_{A_0,Ea_0}}{log10(t)-b_{A_0,Ea_0}}, \mu_{T_0}, \sigma_{T_0}\right)\right)'$

$$f(t) = -\left(\frac{a_{A_0,Ea_0}}{log10(t) - b_{A_0,Ea_0}}\right)'\phi\left(\frac{a_{A_0,Ea_0}}{log10(t) - b_{A_0,Ea_0}}, \mu_{T_0}, \sigma_{T_0}\right)$$

$$f(t) = \frac{a_{A_0,Ea_0}ln(10)}{t\left(b_{A_0,Ea_0}ln(10) - ln(t)\right)^2}\phi\left(\frac{a_{A_0,Ea_0}}{log10(t) - b_{A_0,Ea_0}}, \mu_{T_0}, \sigma_{T_0}\right)$$

We can also compute the quantiles tc_{25}, tc_{50} and tc_{75} (with $F(tc_{25}) = 0.25$, $F(tc_{50}) = 0.50$ and $F(tc_{75}) = 0.75$) and $p_c = p(tc < 30s) = F(30)$ which is the probability that the thermal runaway delay would be so small that it would be very hard for someone to step in.

We have $0.25 = p(tc \leq tc_{25}) = 1 - \Phi\left(\frac{a_{A_0,Ea_0}}{log10(tc_{25}) - b_{A_0,Ea_0}}, \mu_{T_0}, \sigma_{T_0}\right)$

$$\Phi\left(\frac{a_{A_0,Ea_0}}{log10(tc_{25}) - b_{A_0,Ea_0}}, \mu_{T_0}, \sigma_{T_0}\right) = 0.75.$$

We thus have $\frac{a_{A_0,Ea_0}}{log10(tc_{25}) - b_{A_0,Ea_0}} = Z_{0.75}(\mu_{T_0}, \sigma_{T_0})$, where $Z_{0.75}(\mu_{T_0}, \sigma_{T_0})$ is a quantile of $N(\mu_{T_0}, \sigma_{T_0})$.

This leads to $tc_{25} = 10^{\frac{a_{A_0,Ea_0}}{Z_{0.75}(\mu_{T_0},\sigma_{T_0})} + b_{A_0,Ea_0}}$. Likewise, we have

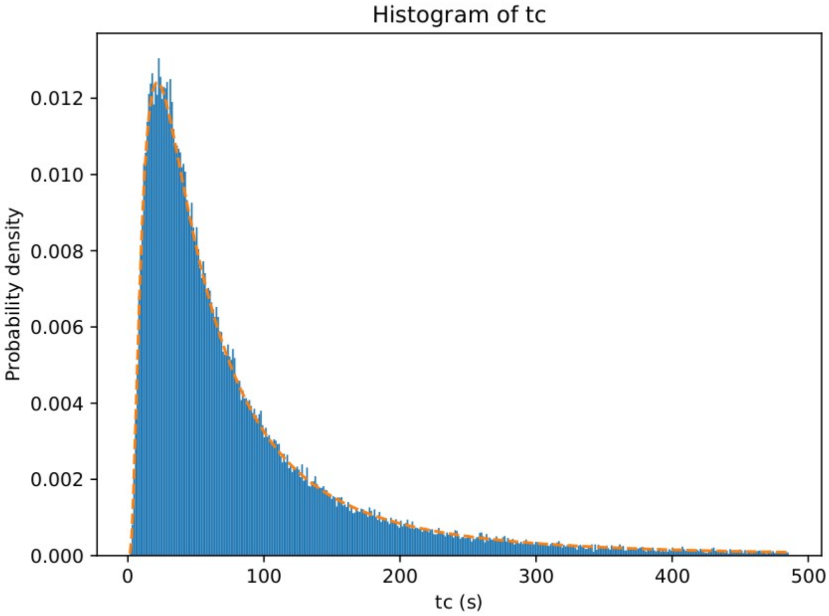
$tc_{75} = 10^{\frac{a_{A_0,Ea_0}}{Z_{0.25}(\mu_{T_0},\sigma_{T_0})} + b_{A_0,Ea_0}}$ and $tc_{50} = 10^{\frac{a_{A_0,Ea_0}}{Z_{0.50}(\mu_{T_0},\sigma_{T_0})} + b_{A_0,Ea_0}}$.

Of course, these formula are also valid for any $A \in [A_{min}, A_{max}]$ and $Ea \in [Ea_{min}, Ea_{max}]$.

We compared the analytical functions with an histogram obtained by generating 10,000 values of $T_0 \sim N(\mu_{T_0} = 525K, \sigma_{T_0} = 20K)$ and computing the corresponding *tc* for (A, Ea) via the two linear interpolations. We obtained the following results:

***A* = 8.6E+11 (mol, cm, s) - *Ea* = 30 kcal/mol**	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
Analytical	28.84	55.04	108.68	0.2636
Numerical	28.94	54.94	107.72	0.2625

Figure 4:



Probability distribution for A_0 = **8.6E+11** *and Ea_0 =* **30**

We also computed the probability distribution for two other (*A*, *Ea*) chosen randomly.

***A* = 6.14E+12 - *Ea* = 37.36 kcal/mol**	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
Analytical	3109.14	7071.60	16797.92	7.75E-08
Numerical	3099.12	7069.12	16815.32	0

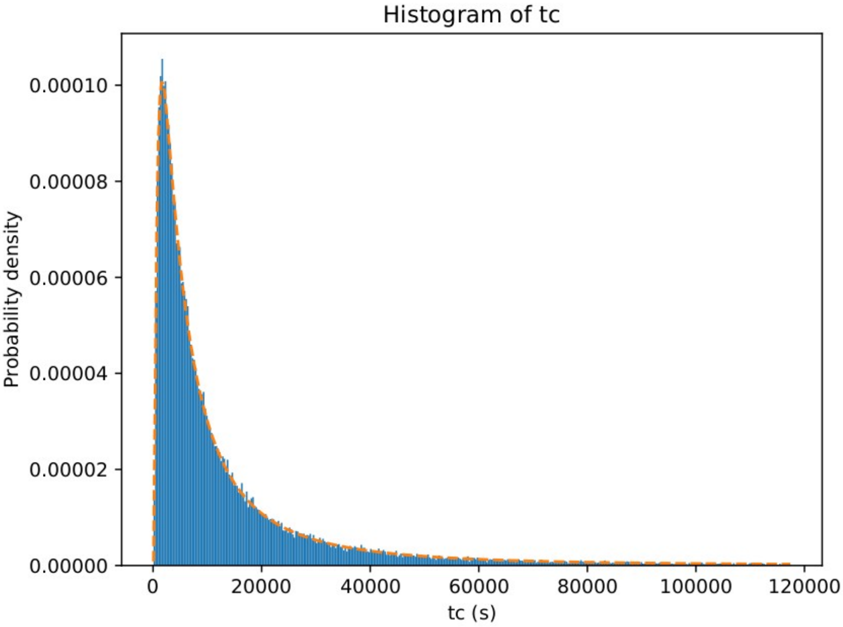
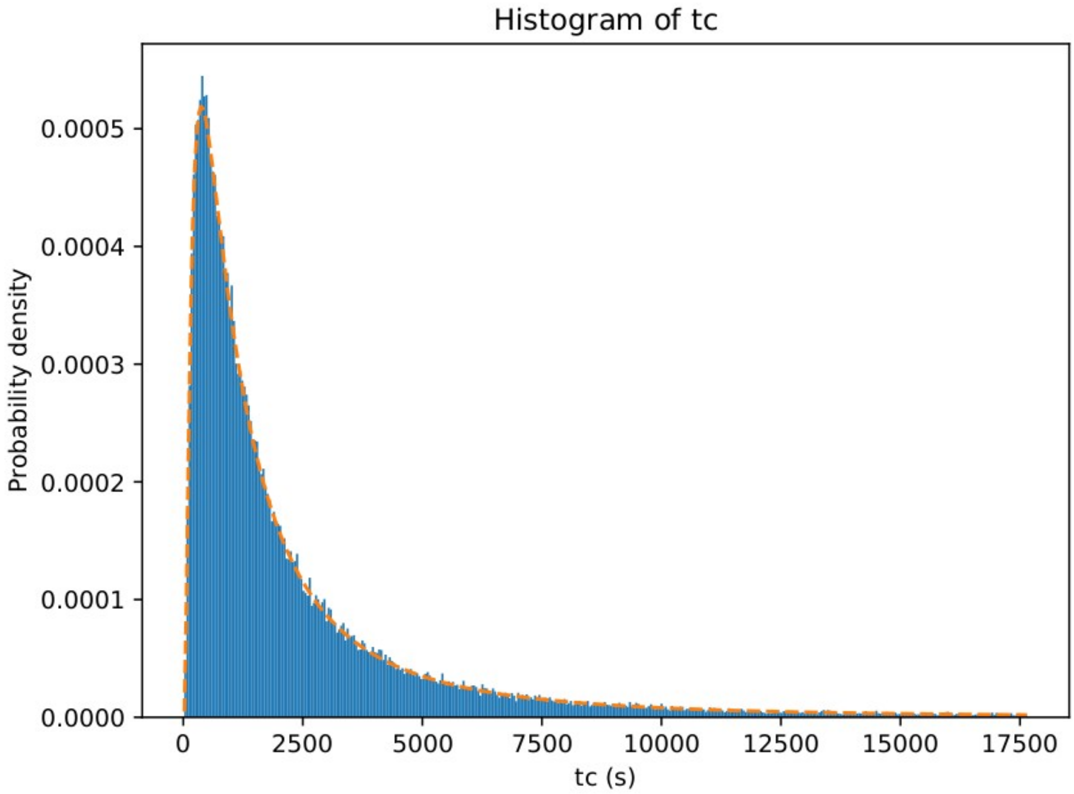


Figure 5: Probability distribution for A = **6.14E+12** *and Ea =* **37.36**

***A* = 3.06E+12 - *Ea* = 34.82 kcal/mol**	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
Analytical	625.17	1336.97	2976.44	8.66E-05
Numerical	625.34	1340.69	2990.27	9.00E-05

Figure 6:



Probability distribution for A = **3.06E+12** *and Ea =* **34.82**

***A* = 2.99E+13 - *Ea* = 43.18 kcal/mol**	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
Analytical	1.24E+05	3.24E+05	8.86E+05	0
Numerical	1.24E+05	3.20E+05	8.84E+05	0

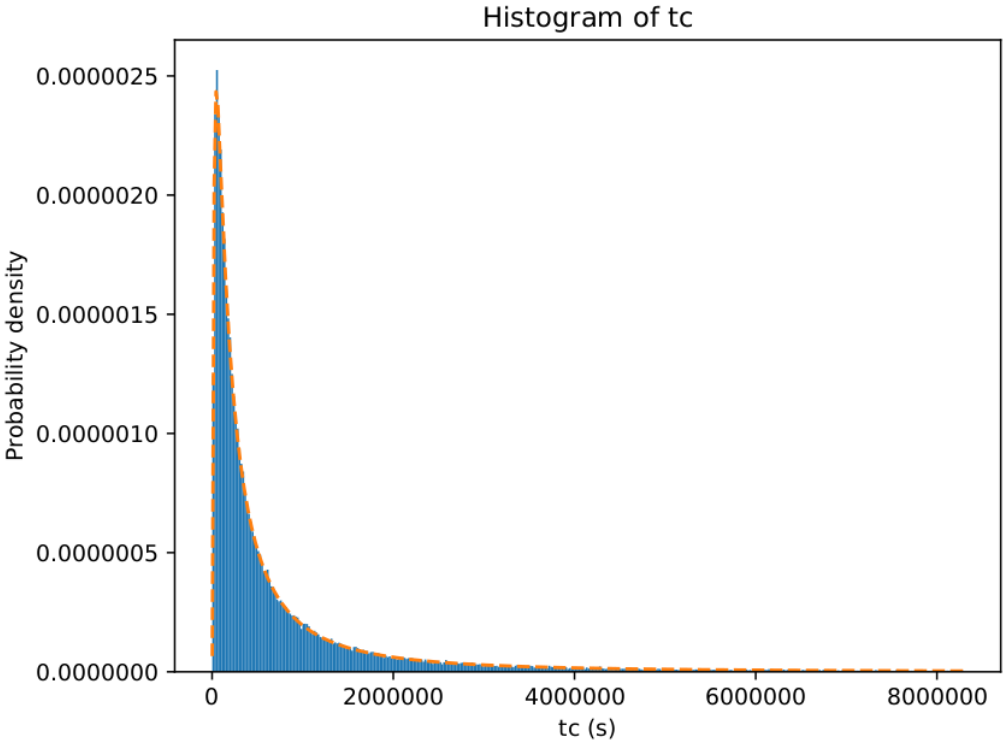


Figure 7: Probability distribution for A = **2.99E+13** *and Ea =* **43.18**

Tests performed with other parameter values led to an equally satisfying agreement, thereby validating the analytical formula.

[1] N.N. Semenov, Thermal theory of combustion and explosion, Natl. Advis. Comm. Aeronaut. -- Tech. Memo. (1942) 52-.

[2] C.K. Westbrook, F.L. Dryer, Simplified reaction mechanisms for the oxidation of hydrocarbon fuels in flames, Combust. Sci. Technol. 27 (1981) 31–43.

[3] R.J. Reed, North American Combustion Handbook, vol. 1: Combustion, Fuels, Stoichiometry, Heat Transf. Fluid Flow. (1986).

[4] D.G. Goodwin, Cantera C++ user’s guide, Calif. Inst. Technol. (2002).

Appendix B: priors

In order to perform the imprecise Bayesian analysis, we decided to use sixth priors which are uniform with respect to the following variables:

- first prior: *log10(A) - Ea*
- second prior: *A – Ea*
- third prior: *1/log10(A) - Ea*
- fourth prior: *1/log10(A) – 1/Ea*
- fifth prior: *1/A – Ea*
- sixth prior: *A – 1/Ea*

Let us pose $x = log10(A)$. Let us first consider the univariate priors $f_{log10(A)}$, $f_{\frac{1}{log10(A)}}$, f_A, $f_{\frac{1}{A}}$, f_{Ea}, $f_{\frac{1}{Ea}}$ which are uniform with respect to the indexed variables. We shall express the corresponding cumulative distribution functions and then the pdf with respect to *x* and *Ea*.

We straightforwardly have $f_{log10(A)}(log10(A)) = \dfrac{1}{log10(A_{max}) - log10(A_{min})}$ and $f_{Ea}(Ea) = \dfrac{1}{Ea_{max} - Ea_{min}}$.

For $f_{\frac{1}{log10(A)}}$**,** we have $F_{\frac{1}{log10(A)}}(x) = p\left(log10(A) \le x\right) = p\left(\dfrac{1}{log10(A)} \ge \dfrac{1}{x}\right) = 1 - F_{\frac{1}{log10(A)}}\left(\dfrac{1}{x}\right)$

$$F_{\frac{1}{log10(A)}}(x) = 1 - \frac{1}{\frac{1}{log10(A_{min})} - \frac{1}{log10(A_{max})}}\left(\frac{1}{x} - \frac{1}{log10(A_{max})}\right)$$

$$f_{\frac{1}{log10(A)}}(x) = \frac{1}{\frac{1}{log10(A_{min})} - \frac{1}{log10(A_{max})}}\,\frac{1}{x^2}$$

$$\rightarrow f_{\frac{1}{log10(A)}}\left(log10(A)\right) = \frac{1}{\frac{1}{log10(A_{min})} - \frac{1}{log10(A_{max})}}\,\frac{1}{log10(A)^2}$$

For f_A, we have $F_A(x) = \dfrac{10^x - A_{min}}{A_{max} - A_{min}} \rightarrow f_A(x) = \dfrac{ln(10)10^x}{A_{max} - A_{min}}$,

$$f_A\left(log10(A)\right) = \frac{ln(10)10^{log10(A)}}{A_{max} - A_{min}}.$$

For $f_{\frac{1}{A}}$, we have

$$F_{\frac{1}{A}}(x) = \mathrm{p}\ \left(log10(A) \le x\right) = p\left(A \le 10^x\right) = \mathrm{p}\ \left(\tfrac{1}{A} \ge \tfrac{1}{10^x}\right) = 1 - F_{\frac{1}{A}}\left(\tfrac{1}{10^x}\right)$$

$$\mathrm{F}_{\frac{1}{A}}(x) = 1 - \frac{\frac{1}{10^x} - \frac{1}{A_{max}}}{\frac{1}{A_{min}} - \frac{1}{A_{max}}} \rightarrow \mathrm{f}_{\frac{1}{A}}(x) = \frac{ln(10)10^{-x}}{\frac{1}{A_{min}} - \frac{1}{A_{max}}} \rightarrow \mathrm{f}_{\frac{1}{A}}\left(log10(A)\right) = \frac{ln(10)10^{-log10(A)}}{\frac{1}{A_{min}} - \frac{1}{A_{max}}}$$

$$F_{\frac{1}{Ea}}(Ea) = 1 - \frac{\frac{1}{Ea} - \frac{1}{Ea_{max}}}{\frac{1}{Ea_{min}} - \frac{1}{Ea_{max}}} \rightarrow f_{\frac{1}{Ea}}(Ea) = \frac{1}{Ea^2}\frac{1}{\frac{1}{Ea_{min}} - \frac{1}{Ea_{max}}}.$$

For the first prior (uniform with respect to *log10(A)* and *Ea),* we have

$$f_{0,1}(log10(A), Ea) = f_{log10(A),Ea}(log10(A), Ea) = f_{log10(A)}\big(log10(A)\big) f_{Ea}(Ea)$$

$$f_{0,1}(log10(A), Ea) = \frac{1}{log10(A_{max}) - log10(A_{min})}\frac{1}{Ea_{max} - Ea_{min}}$$

For the second prior (uniform with respect to A and *Ea),* we have

$$f_{0,2}(log10(A), Ea) = f_{A,Ea}(log10(A), Ea) = f_{A}\big(log10(A)\big) f_{Ea}(Ea)$$

$$f_{0,2}(log10(A), Ea) = \frac{ln(10)}{A_{max} - A_{min}}\frac{1}{Ea_{max} - Ea_{min}}10^{log10(A)}$$

For the third prior (uniform with respect to *1/log10(A)* and *Ea),* we have

$$f_{0,3}(log10(A), Ea) = f_{\frac{1}{log10(A)},Ea}(log10(A), Ea) = f_{\frac{1}{log10(A)}}\big(log10(A)\big) f_{Ea}(Ea)$$

$$f_{0,3}(log10(A), Ea) = \frac{1}{\frac{1}{log10(A_{min})} - \frac{1}{log10(A_{max})}}\frac{1}{Ea_{max} - Ea_{min}}\frac{1}{log10(A)^2}$$

For the fourth prior (uniform with respect to *1/log10(A)* and *1/Ea),* we have

$$f_{0,4}(log10(A), Ea) = f_{\frac{1}{log10(A)},\frac{1}{Ea}}(log10(A), Ea) = f_{\frac{1}{log10(A)}}\big(log10(A)\big) f_{\frac{1}{Ea}}(Ea)$$

$$f_{0,4}(log10(A), Ea) = \frac{1}{\frac{1}{log10(A_{min})} - \frac{1}{log10(A_{max})}}\frac{1}{\frac{1}{Ea_{min}} - \frac{1}{Ea_{max}}}\frac{1}{log10(A)^2}\frac{1}{Ea^2}$$

For the fifth prior (uniform with respect to *1/A* and *Ea),* we have

$$f_{0,5}(log10(A), Ea) = f_{\frac{1}{A},Ea}(log10(A), Ea) = f_{\frac{1}{A}}\big(log10(A)\big) f_{Ea}(Ea)$$

$$f_{0,5}(log10(A), Ea) = \frac{ln(10)}{\frac{1}{A_{min}} - \frac{1}{A_{max}}}\frac{1}{Ea_{max} - Ea_{min}}10^{-log10(A)}$$

For the sixth prior (uniform with respect to *A* and *1/Ea),* we have

$$f_{0,6}(log10(A), Ea) = f_{A,\frac{1}{Ea}}(log10(A), Ea) = f_{A}\big(log10(A)\big) f_{\frac{1}{Ea}}(Ea)$$

$$f_{0,6}(log10(A), Ea) = \frac{ln(10)}{A_{max} - A_{min}}\frac{1}{\frac{1}{Ea_{min}} - \frac{1}{Ea_{max}}}10^{log10(A)}\frac{1}{Ea^2}$$

The six priors are shown in the following figures.

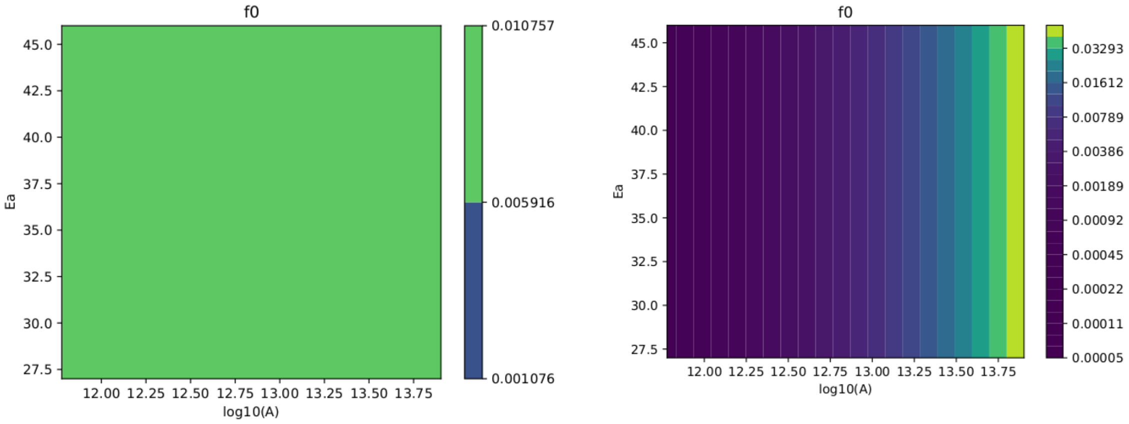


Figure 1: $f_{0,1}(log10(A), Ea) = f_{log10(A),Ea}(log10(A), Ea)$ - $f_{0,2}(log10(A), Ea) = f_{A,Ea}(log10(A), Ea)$

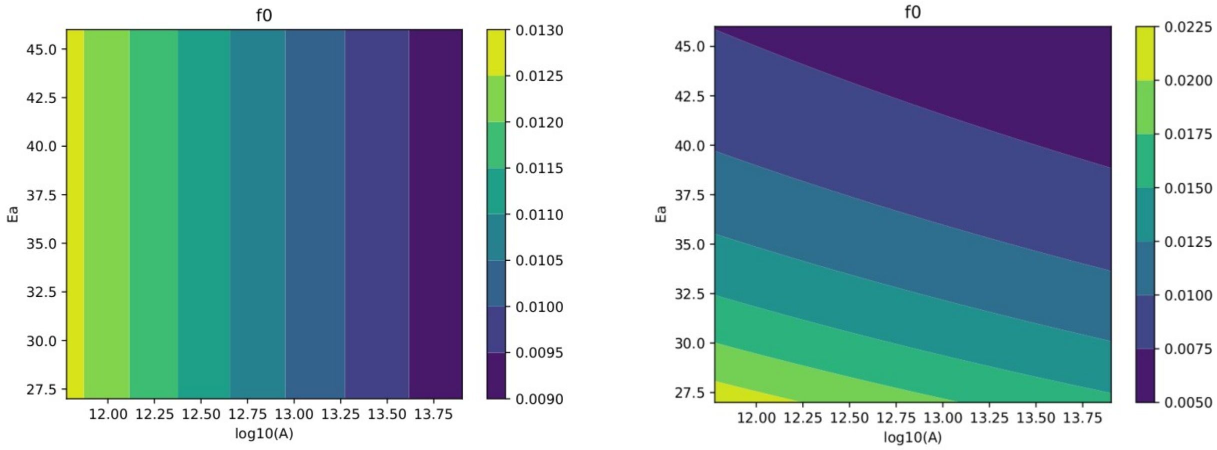


Figure 2: $f_{0,3}(log10(A), Ea) = f_{\frac{1}{log10(A)},Ea}(log10(A), Ea)$ - $f_{0,4}(log10(A), Ea) = f_{\frac{1}{log10(A)},\frac{1}{Ea}}(log10(A), Ea)$

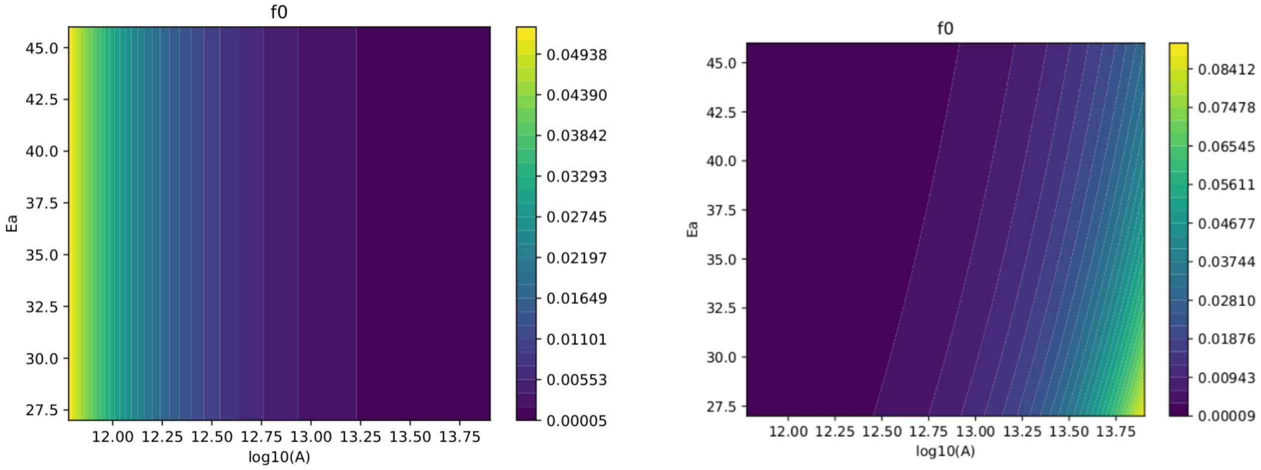


Figure 3: $f_{0,5}(log10(A), Ea) = f_{\frac{1}{A},Ea}(log10(A), Ea)$ - $f_{0,6}(log10(A), Ea) = f_{A,\frac{1}{Ea}}(log10(A), Ea)$

The integrals of the priors were computed over $A \in [6.0\text{E}{+}11\ ;\ 8.0\text{E}{+}13]$ mol/m^3/s and $Ea \in [27; 46]$.

Prior	$f_{0,1}$	$f_{0,2}$	$f_{0,3}$	$f_{0,4}$	$f_{0,5}$	$f_{0,6}$
Integral	1.00100075	1.00100422	1.00100064	1.00114586	1.00100054	1.00114796

Appendix C: virtual experimental data

We created “experimental” data allowing us to determine posterior probability distributions of *A* and *Ea*.
We considered a constant-volume reactor at atmospheric pressure with a very diluted mixture of propane and oxygen: X_{C3H8} = 1E-05, X_{O2} = 5E-05 and X_{N2} = 0.99994.
Under such a high dilution, the temperature remains nearly constant so that analytical expressions of the profile of $X_{C3H8}(t)$ are available. It has been rigorously verified that they are virtually identical to the numerical results of Cantera.
Using the “true” values A_0 = 8.60E+11 and Ea_0 = 30.00 kcal/mol, we generated mole fraction profiles of C_3H_8 at four different temperatures in the range [1135; 2249] K. We used the model described in subsection 2.1 of the article and in appendix A.
We then randomly chose several time points t_i and generated normally distributed noise in such a way that $X_{C_3H_8,exp}(t_i) = X_{C_3H_8}(t_i) + \epsilon_i$ and $\epsilon_i \sim N\left(0, \sigma_r . X_{C3H8}(t_i)\right)$. σ_r is the relative standard deviation. The profile of propane $X_{C3H8}(t)$ has always been computed with A_0 and Ea_0.

We considered four situations:

A) we have no data whatsoever, we only know that $A \in [6.0\text{E}{+}11; 8.0\text{E}{+}13]$ mol/m^3/s and $Ea \in [27; 46]$ kcal/mol.
B) We have one profile of C_3H_8 with 6 time points measured at 1845 K with σ_r = 25%.
C) We have two profiles of C_3H_8 with 6 time points measured at 1135 K and 2249 K with σ_r = 25%.
D) We have four profiles of C_3H_8 with 10 time points measured at 1135 K, 1478 K, 1845 K, and 2249 K with σ_r = 6%.

The different profiles are shown in the figures below.

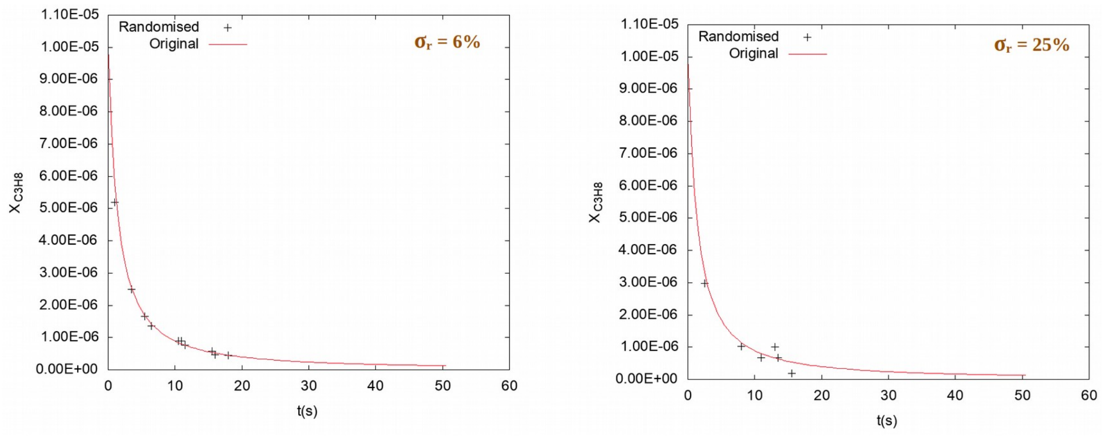


Figure 1: T_0 = 1135 K.

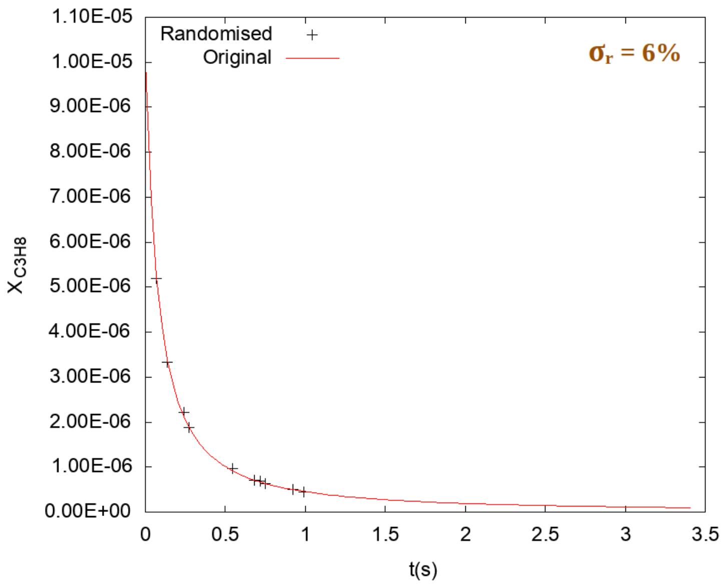


Figure 2: T_0 *= 1478 K.*

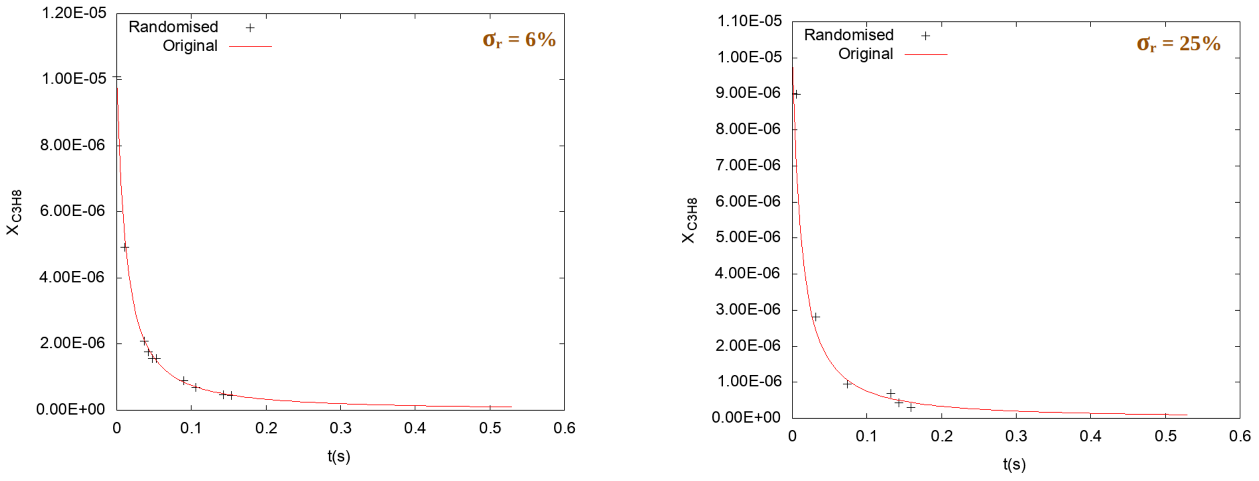


Figure 3: T_0 *= 1845 K.*

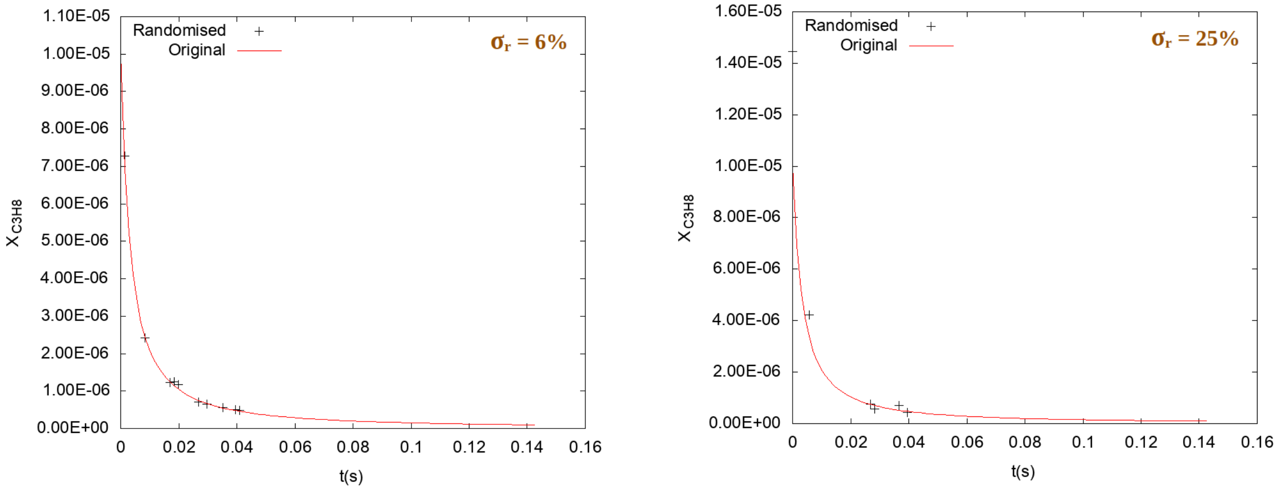


Figure 4: T_0 =2249 K.

The likelihood of the experimental data given the parameters is:

$$L(data|A,Ea)=\prod_{i=1}^{m}\prod_{j=1}^{n_{t,i}}\frac{1}{\sqrt{2\pi\sigma_{i,j}^2}}exp\left(-\frac{1}{2\sigma_{i,j}^2}\left(X_{C3H8,i}(t_j,A,Ea)-X_{C3H8,exp,i}(t_j)\right)^2\right)$$

where *m* is the number of experiments, $n_{t,i}$ is the number of time points for the *i*-th experiment and $\sigma_{i,j}=\sigma_{r,i}X_{C3H8,i}(t_j,A_0,Ea_0)$ is the local standard deviation.

The log-likelihood is given by

$$l(data|A,Ea)=\sum_{i=1}^{m}\sum_{j=1}^{n_{t,i}}\left(ln(\frac{1}{\sqrt{2\pi\sigma_{i,j}^2}})-\frac{1}{2\sigma_{i,j}^2}\left(X_{C3H8,i}(t_j,A,Ea)-X_{C3H8,exp,i}(t_j)\right)^2\right)$$

$$l(data|A,Ea)=\sum_{i=1}^{m}\sum_{j=1}^{n_{t,i}}\left(-\frac{1}{2}ln(2\pi\sigma_{i,j}^2)-\frac{1}{2\sigma_{i,j}^2}\left(X_{C3H8,i}(t_j,A,Ea)-X_{C3H8,exp,i}(t_j)\right)^2\right)$$

The log-likelihood for situation B, C and D can be visualised in the figures just below. They were all obtained with **300*300** values of *A* and *Ea*.

We can see that the likelihood function becomes sharper and sharper as more precise measurements are used to compute it, which is completely expected.

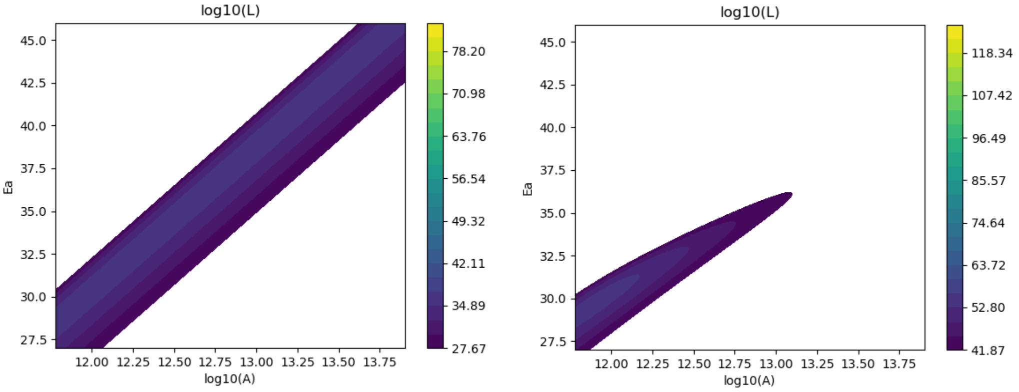


Figure 5: Situation B - Situation C

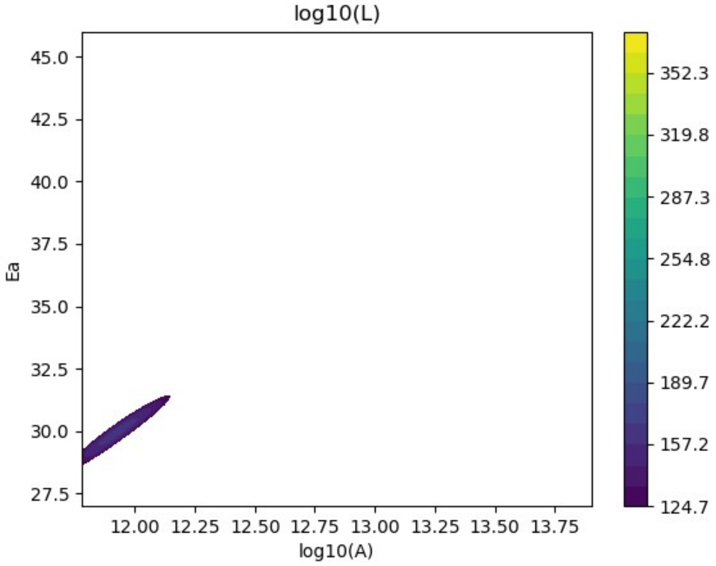


Figure 6: Situation D

For each situation B, C and D, we obtained 6 posteriors based on the six priors mentioned in Appendix B.

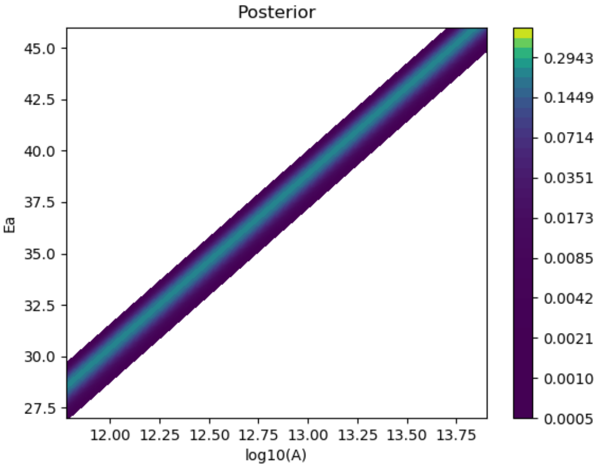
$$f_{B,1}\left(log10(A), Ea\right) = \frac{L\left(B|log10(A), Ea\right) f_{0,1}\left(log10(A), Ea\right)}{\int_{log10(A)} \int_{Ea} L\left(B|log10(A), Ea\right) f_{0,1}\left(log10(A), Ea\right) dlog10(A) dEa}$$

is the posterior based on the first prior $f_{0,1}$ and the experiment B.

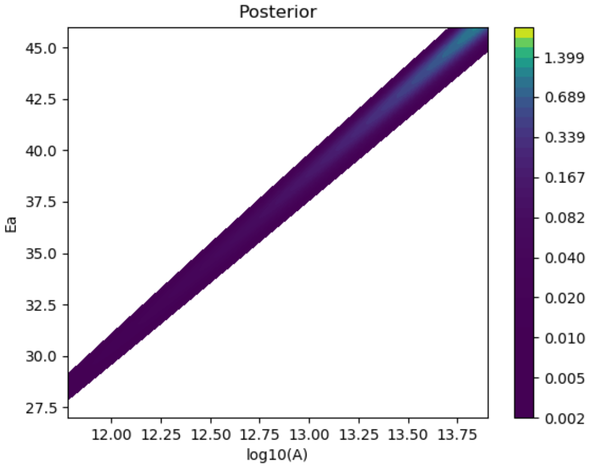
$$f_{C,4}\left(log10(A), Ea\right) = \frac{L\left(C|log10(A), Ea\right) f_{0,4}\left(log10(A), Ea\right)}{\int_{log10(A)} \int_{Ea} L\left(C|log10(A), Ea\right) f_{0,4}\left(log10(A), Ea\right) dlog10(A) dEa}$$

is the posterior based on the fourth prior $f_{0,4}$ and the experiment C.

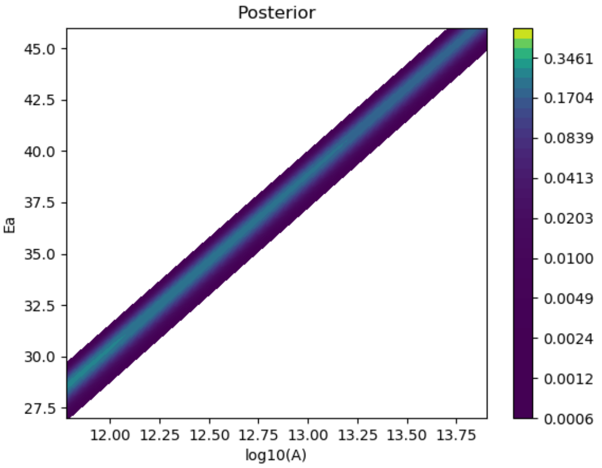
And so on.



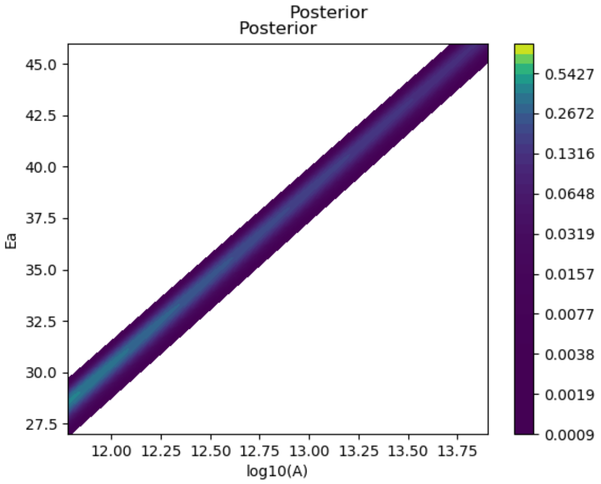
$\mathbf{f_{B,1}}$



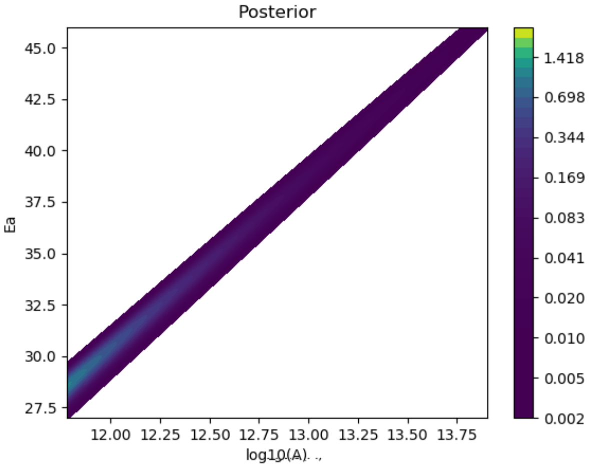
$\mathbf{f_{B,2}}$



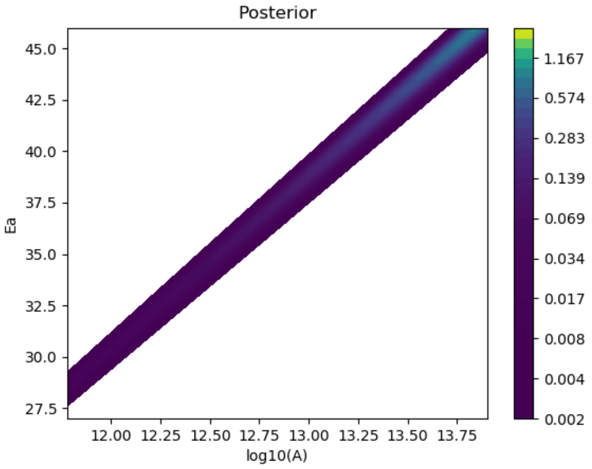
$\mathbf{f_{B,3}}$



$\mathbf{f_{B,4}}$

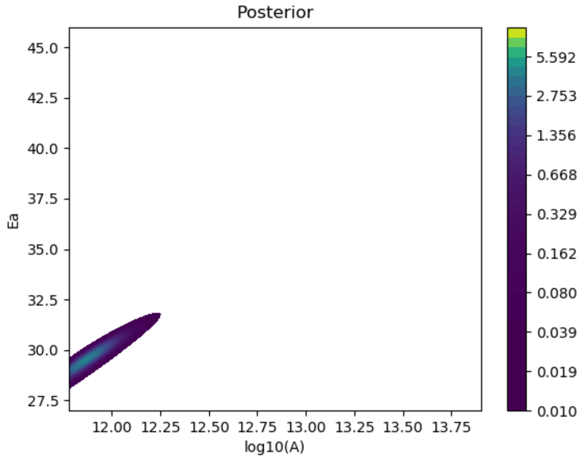


$\mathbf{f_{B,5}}$

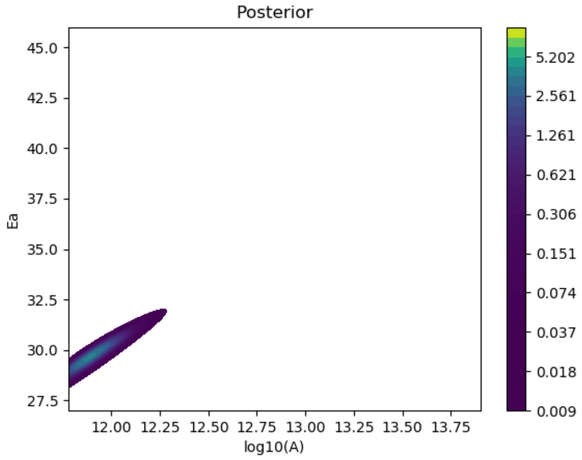


$\mathbf{f_{B,6}}$

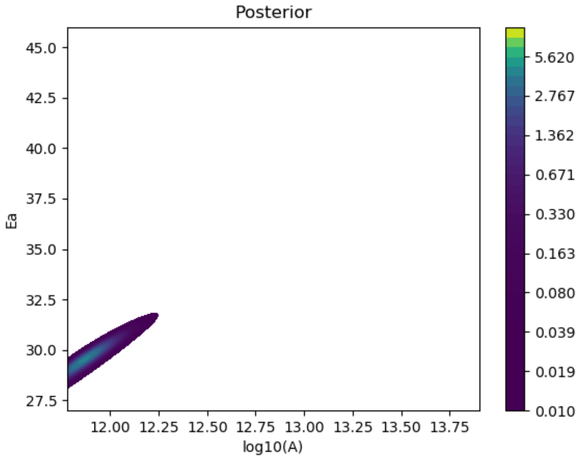
In situation B, *log10(A)* and *Ea* are strongly correlated in most posteriors and many values of (*log10(A)* , *Ea*) are equally compatible with the available evidence.



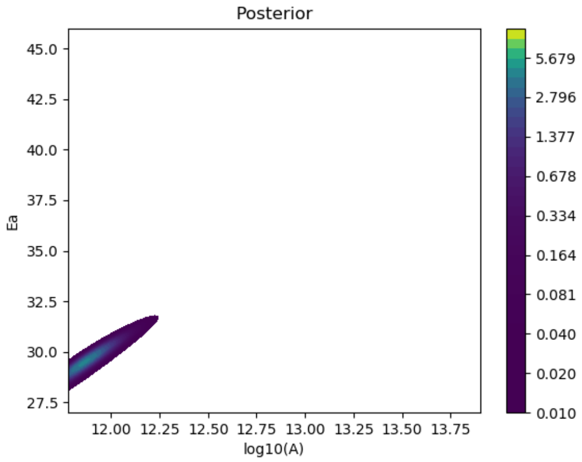
$f_{C,1}$



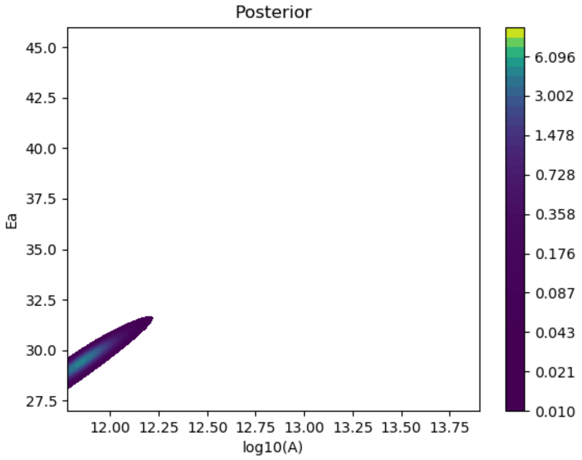
$f_{C,2}$



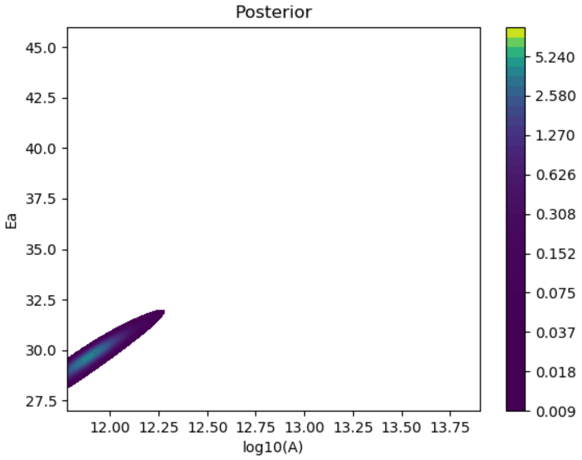
$f_{C,3}$



$f_{C,4}$

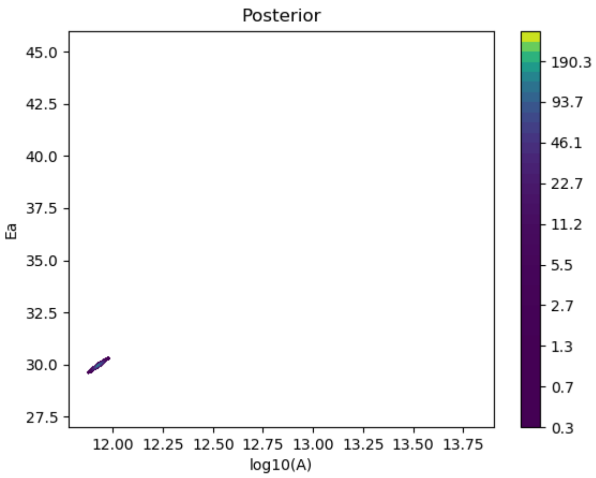


$f_{C,5}$

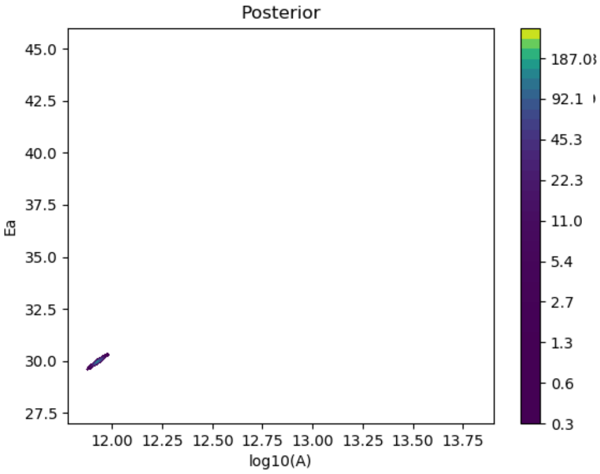


$f_{C,6}$

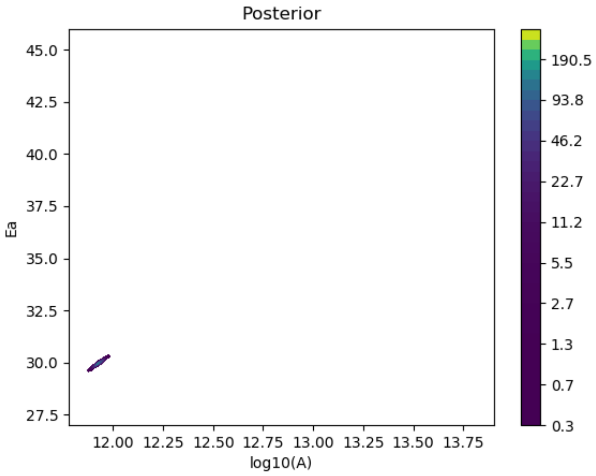
The range of probable parameter values is considerably smaller in situation C but this could still lead to inaccurate predictions.



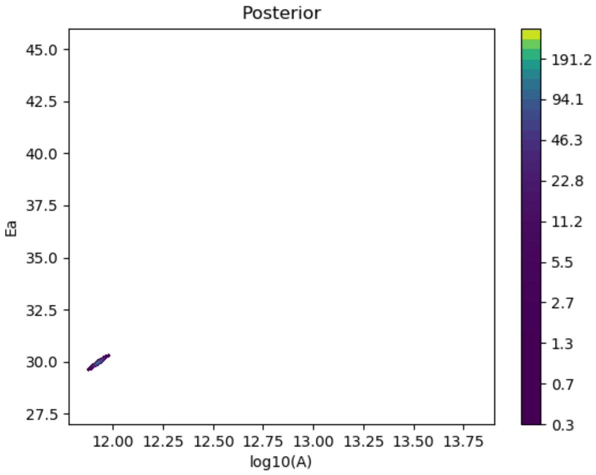
$\mathbf{f}_{D,1}$



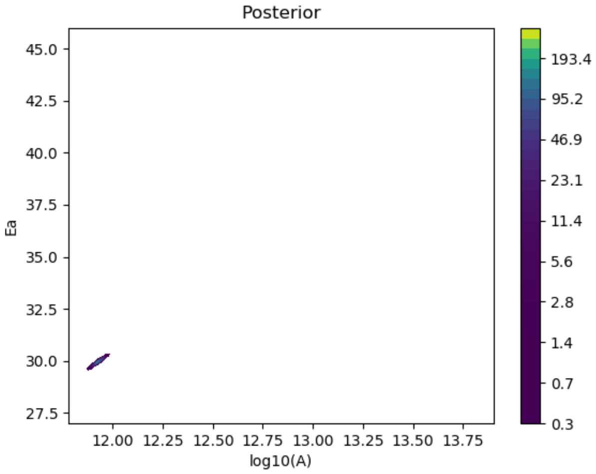
$\mathbf{f}_{D,2}$



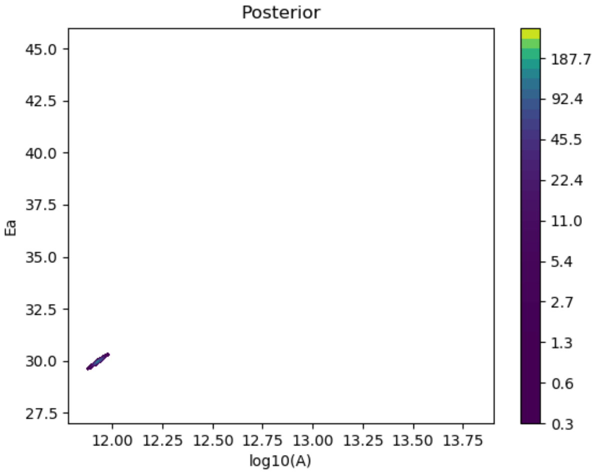
$\mathbf{f}_{D,3}$



$\mathbf{f}_{D,4}$



$\mathbf{f}_{D,5}$



$\mathbf{f}_{D,6}$

The range of probable parameter values is very small in situation D in all posteriors, which means that the parameters are known with a high degree of accuracy.

Appendix D: Bayesian estimation of the delay time distribution

We are interested in how quickly the mixture reaches the critical temperature *Tc* = 766 K beyond which it would be impossible for a technician to intervene to stop the explosion. *tc* is the critical delay time defined as $T(tc) = T_c$. As explained in appendix A, the initial temperature follows a normal distribution $T_0 \sim N(\mu_{T_0} = 524K, \sigma_{T_0} = 20K)$. We can limit ourselves to the interval $[T_{0,min} = 440$ K; $T_{0,max} = 600$ K] as $p(T < T_{0,min} \cup T > T_{0,max})$ < 2E-04.
The true values of the kinetic parameters are A_0 = 8.6E+11 and Ea_0 = 30.0.

We suppose they are unknown to the safety engineer so that $A \in [6.0\text{E}{+}11\ ;\ 8.0\text{E}{+}13]$ and $Ea \in [27; 46]$ kcal/mol. $tc_{A,Ea}(T_{0,min})$ and $tc_{A,Ea}(T_{0,max})$ can be predicted with a high degree of accuracy thanks to piecewise bilinear interpolation.
It is then possible to predict $tc_{A,Ea}(T_0)$ through a simple linear interpolation:

$log10(tc_{A,Ea}(T_0)) = a_{A,Ea}\frac{1}{T_0} + b_{A,Ea}$ with the coefficients

$a_{A,Ea} = \frac{log10\left(tc_{A,Ea}(T_{0,min})\right) - log10\left(tc_{A,Ea}(T_{0,max})\right)}{1/T_{0,min} - 1/T_{0,max}}$ and

$b_{A,Ea} = log10\left(tc_{A,Ea}(T_{0,min})\right) - a_{A,Ea}\frac{1}{T_{0,min}}$.

For *A* and *Ea*, the probability distribution of t_c is given by

$$f(tc|A, Ea) = \frac{a_{A,Ea}ln(10)}{tc\left(b_{A,Ea}ln(10) - ln(tc)\right)^2}\phi\left(\frac{a_{A,Ea}}{log10(tc) - b_{A,Ea}}, \mu_{T_0}, \sigma_{T_0}\right).$$

We are interested in the quantiles tc_{25}, tc_{50} and tc_{75} which are given by the following formula
$tc_{25} = 10^{\frac{a_{A,Ea}}{Z_{0.75}(\mu_{T_0},\sigma_{T_0})} + b_{A,Ea}}$, $tc_{50} = 10^{\frac{a_{A,Ea}}{Z_{0.50}(\mu_{T_0},\sigma_{T_0})} + b_{A,Ea}}$ and $tc_{75} = 10^{\frac{a_{A,Ea}}{Z_{0.25}(\mu_{T_0},\sigma_{T_0})} + b_{A,Ea}}$

We also want to know $p_c = p(tc < 30s) = F(30)$ which is the probability that the thermal runaway delay would be so small that it would be very hard for a technician to step in.
F is the cumulative probability distribution of t_c given by

$$F(tc|A, Ea) = 1 - \Phi\left(\frac{a_{A,Ea}}{log10(tc) - b_{A,Ea}}, \mu_{T_0}, \sigma_{T_0}\right).$$

For a given (*A*, *Ea*), we can determine $tc_{0.001}$ and $tc_{0.999}$ such that $F(tc_{0.001}|A, Ea) = 0.001$ and $F(tc_{0.999}|A, Ea) = 0.999$.
We have $0.001 = p(tc \leq tc_{0.001}) = 1 - \Phi\left(\frac{a_{A,Ea}}{log10(tc_{0.001}) - b_{A,Ea}}, \mu_{T_0}, \sigma_{T_0}\right)$

$$\Phi\left(\frac{a_{A,Ea}}{log10(tc_{0.001}) - b_{A,Ea}}, \mu_{T_0}, \sigma_{T_0}\right) = 0.999.$$

We thus have $\frac{a_{A,Ea}}{log10(tc_{0.001}) - b_{A,Ea}} = Z_{0.999}(\mu_{T_0}, \sigma_{T_0})$, where $Z_{0.999}(\mu_{T_0}, \sigma_{T_0})$ is a quantile of $N(\mu_{T_0}, \sigma_{T_0})$.

This leads to $tc_{0.001} = 10^{\frac{a_{A,Ea}}{Z_{0.999}(\mu_{T_0},\sigma_{T_0})} + b_{A,Ea}}$. Likewise, $tc_{0.999} = 10^{\frac{a_{A,Ea}}{Z_{0.001}(\mu_{T_0},\sigma_{T_0})} + b_{A,Ea}}$.

The values of the probability density *f(tc)* will then be computed for *n* = 1000 values of *tc* in the interval [$tc_{0.001}$; $tc_{0.999}$].
Given the joint distribution of the parameters (*A*, *Ea*) $f_{A,Ea}$, the distribution of *tc* is given by
$f(tc) = \int_{A\in[A_{min},A_{max}],Ea\in[Ea_{min},Ea_{max}]} f(tc|A,Ea)f_{A,Ea}dAdEa$.
whereby $f_{A,Ea}$ might be either a prior distribution or a posterior distribution after taking the species concentration profiles into account.
We compute it on the interval $[min_{A,Ea}\big(tc(A,Ea)\big), max_{A,Ea}\big(tc(A,Ea)\big)]$.

The true probability distribution of *tc* for A_0 and Ea_0 is as follows:

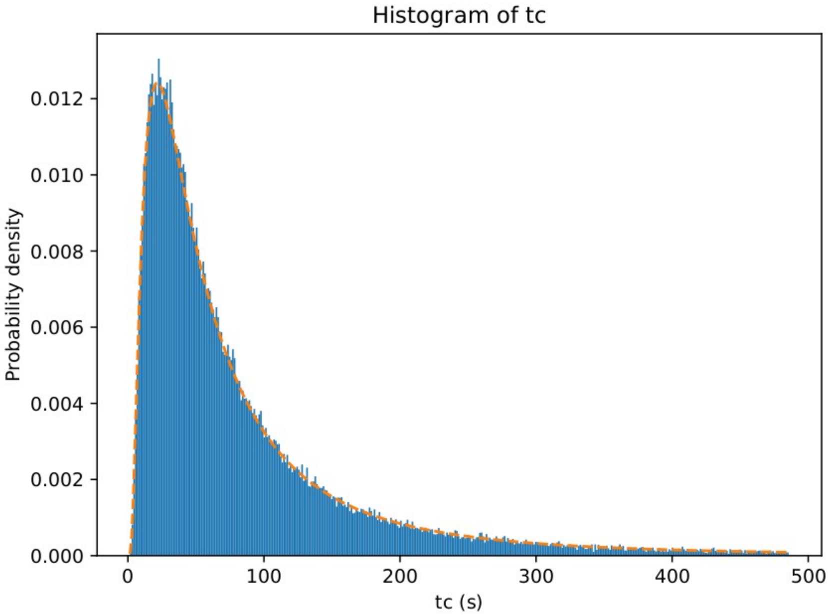
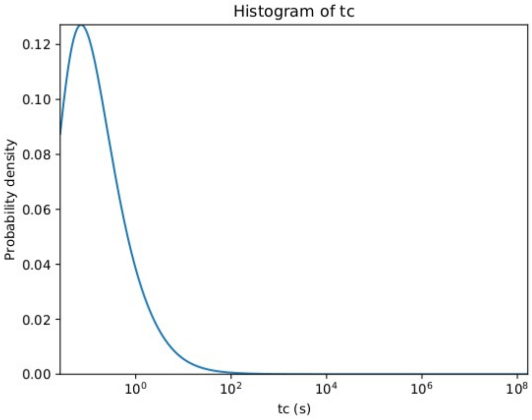


Figure 1: Probability distribution for A_0 = **8.6E+11** *and Ea_0 =* **30**

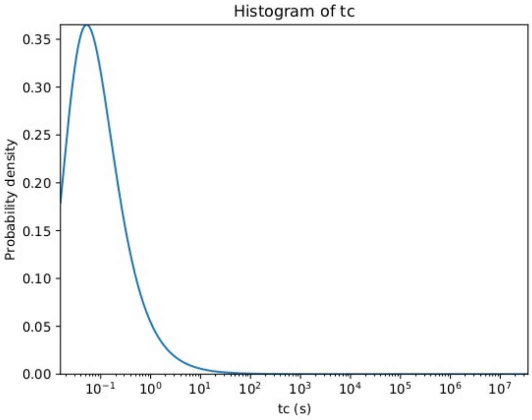
8.6E+11 - 30	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
Analytical	28.86	55.08	108.79	0.2634
Numerical	28.94	54.94	107.72	0.2625

In what follows, *f(tc)* and its main features will be given in Situation A, B, C and D.

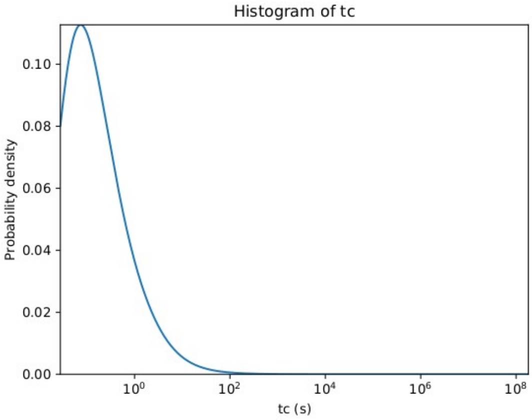
Situation A



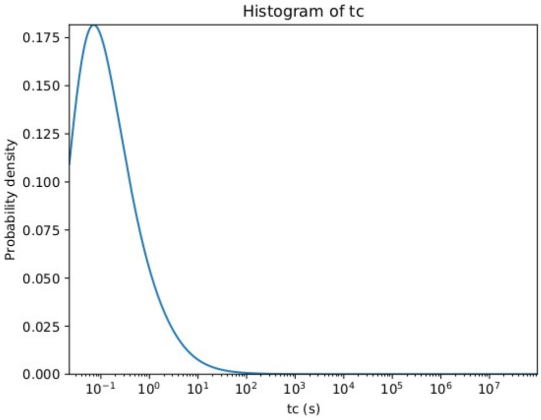
$\mathbf{f_{A,1}}$



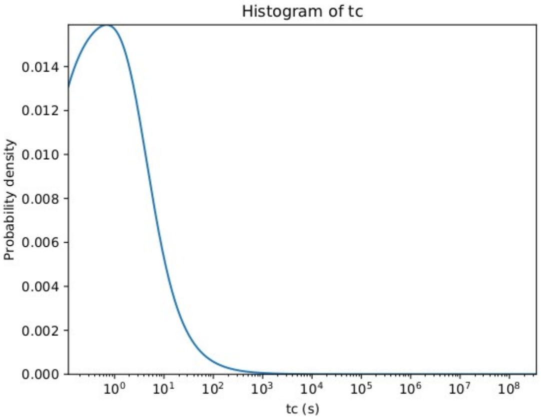
$\mathbf{f_{A,2}}$



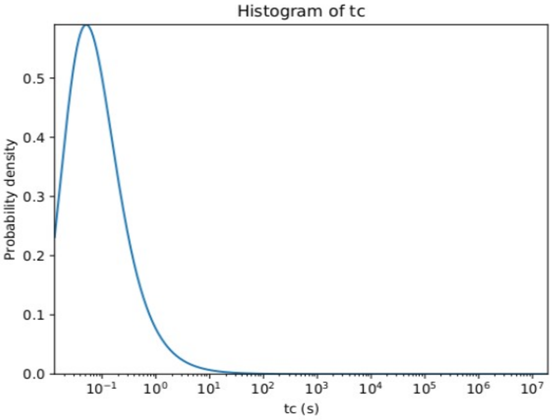
$\mathbf{f_{A,3}}$



$\mathbf{f_{A,4}}$



$\mathbf{f_{A,5}}$

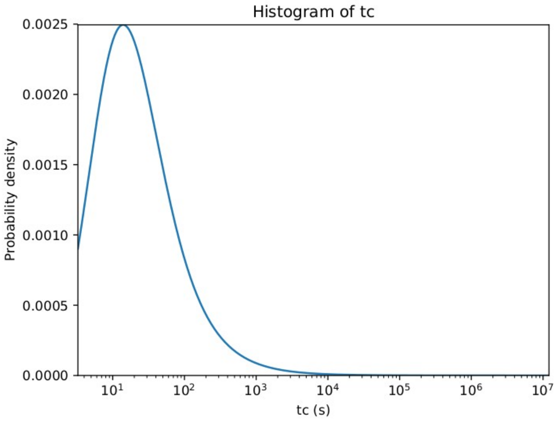


$\mathbf{f_{A,6}}$

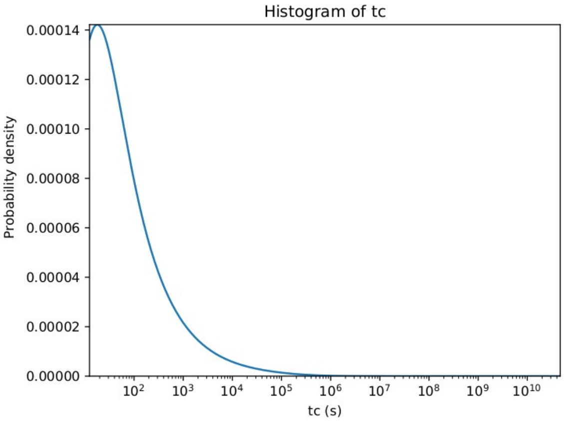
Prior	tc_{25} (s)	tc_{50} (s)	tc_{75} (s)	$p_{critical}$
A_0, Ea_0	**28.86**	**55.08**	**108.79**	**0.2634**
$f_{0,1}$	34.29	2801.66	2.34E+05	0.2424
$f_{0,2}$	7.85	649.06	5.45E+04	0.3260
$f_{0,3}$	39.22	3201.74	2.68E+05	0.2348
$f_{0,4}$	9.39	356.02	4.00E+04	0.3360
$f_{0,5}$	149.45	1.21E+04	9.99E+05	0.1585
$f_{0,6}$	1.80	69.51	8019.06	0.4476
[min; max]	**[1.80; 149.45]**	**[69.51;1.21E+04]**	**[8019.06;9.99E+05]**	**[0.1585;0.4476]**

As could be expected, $f(tc)$ and its features widely differ if the non-updated priors $f_{0,i}(A,Ea)$ are used and none of the $f(tc)$ are close to the true distribution obtained with A_0 and Ea_0.

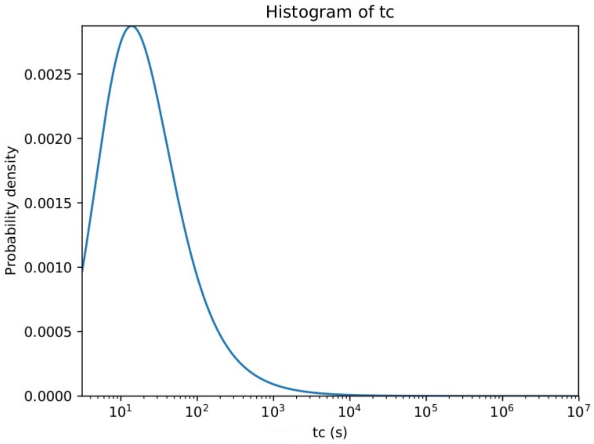
Situation B



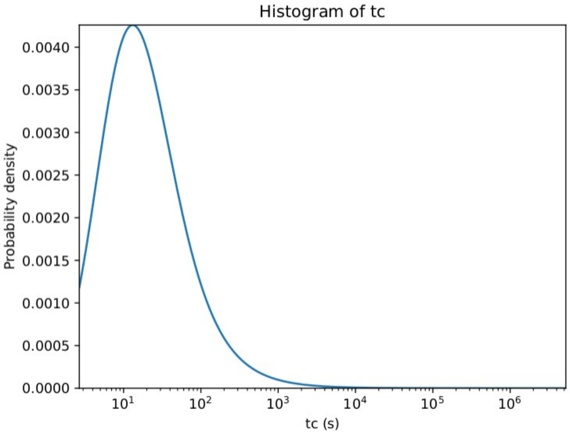
$f_{B,1}$



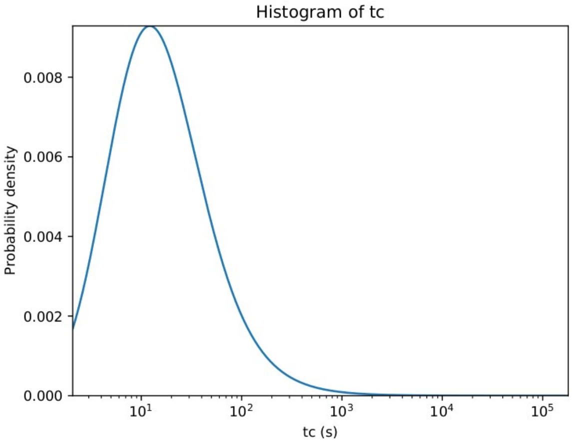
$f_{B,2}$



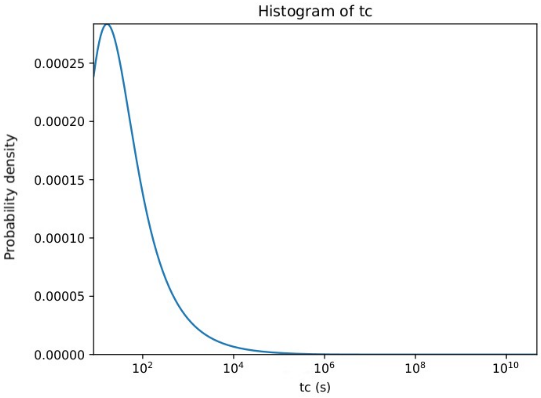
$f_{B,3}$



$f_{B,4}$



$f_{B,5}$

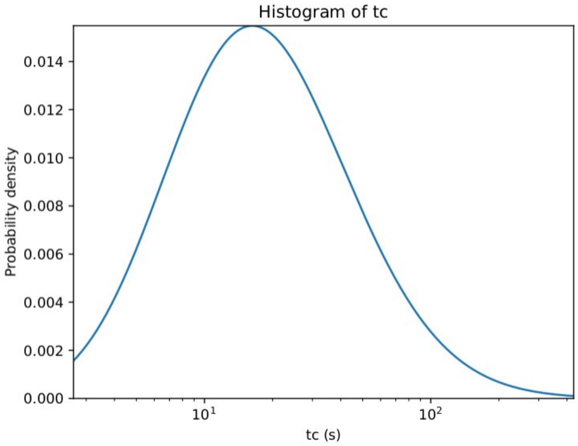


$f_{B,6}$

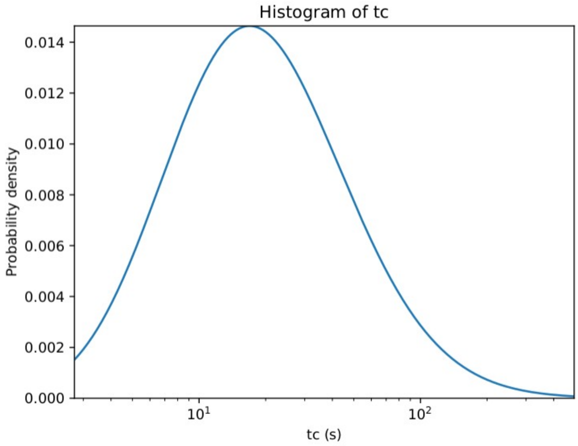
Posterior	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
A_0, Ea_0	**28.86**	**55.08**	**108.79**	**0.2634**
$f_{B,1}$	322.64	5667.50	101985.48	0.0600
$f_{B,2}$	46135.45	267339.01	1194153.91	0.0034
$f_{B,3}$	234.54	3630.43	71792.60	0.0690
$f_{B,4}$	108.43	1035.65	21514.09	0.1018
$f_{B,5}$	35.05	114.69	604.56	0.2183
$f_{B,6}$	26002.85	192780.68	959438.88	0.0069
[min;max]	**[35.05;4.61E+04]**	**[114.69;2.67E+05]**	**[604.56;1.19E+06]**	**[3.4E-03;0.2183]**

As can be seen in **Appendix C: virtual experimental data** (fischer21c-supp.pdf), the use of only one experiment at a single temperature is not enough to determine the two kinetic parameters *A* and *Ea* at the same time. A very large number of (*A*, *Ea*) values are equally probable. Consequently, the probability distribution of *tc* obtained with most posteriors tends to be far off from the real one and the computed distributions themselves strongly disagree with one another.

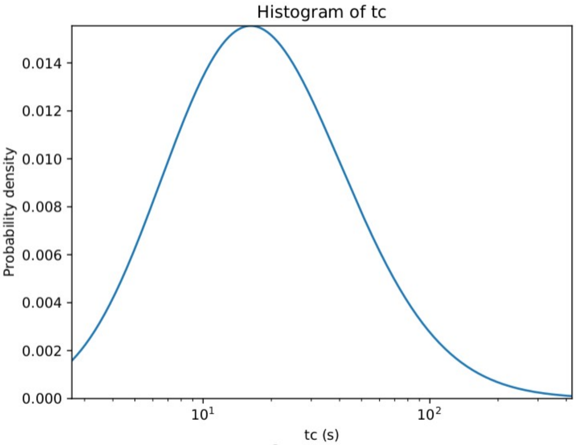
Situation C



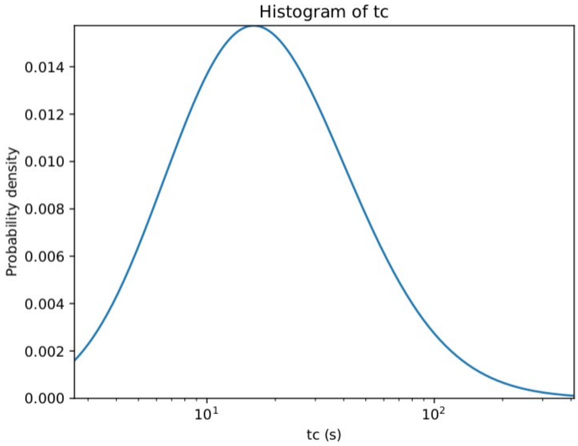
$\mathbf{f}_{\mathbf{C,1}}$



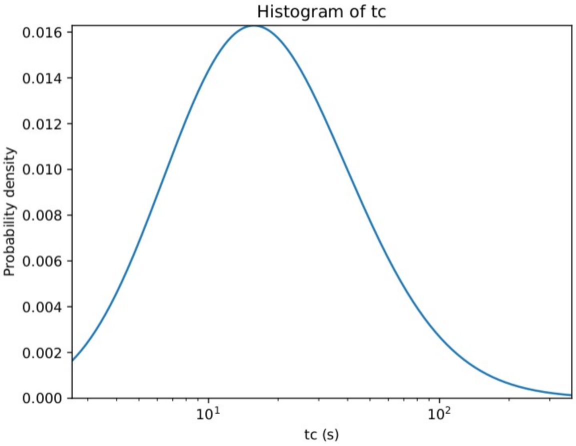
$\mathbf{f}_{\mathbf{C,2}}$



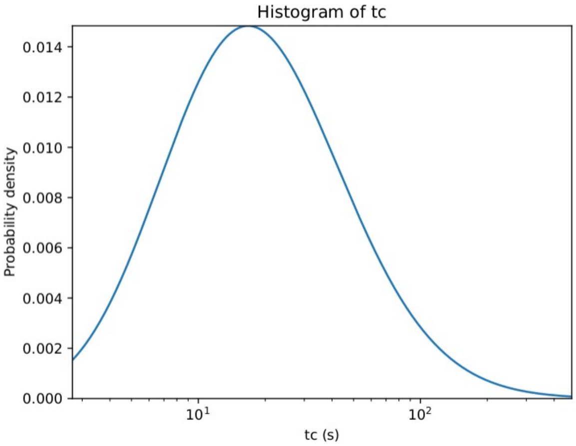
$\mathbf{f}_{\mathbf{C,3}}$



$\mathbf{f}_{\mathbf{C,4}}$



$\mathbf{f}_{\mathbf{C,5}}$

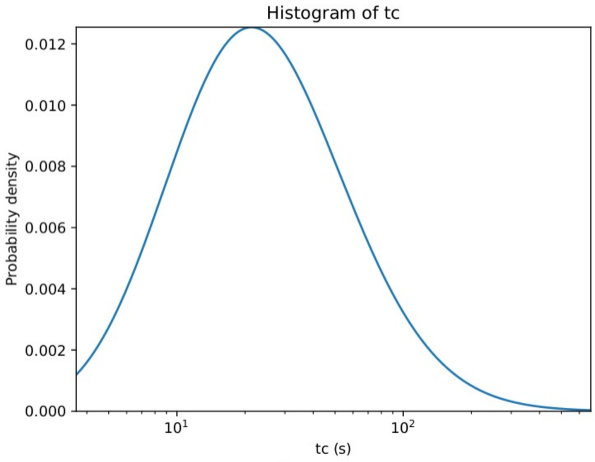


$\mathbf{f}_{\mathbf{C,6}}$

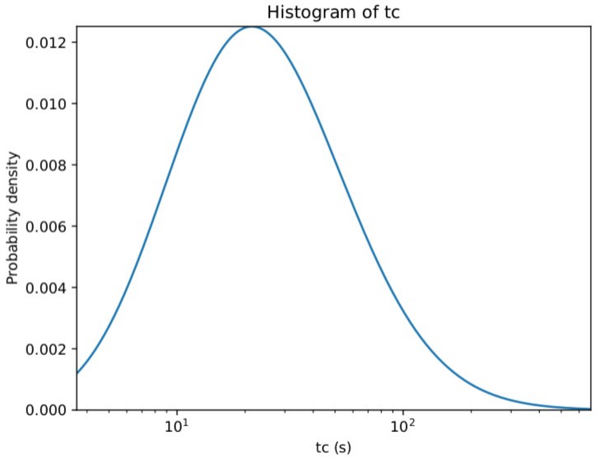
Posterior	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
A_0, Ea_0	**28.86**	**55.08**	**108.79**	**0.2634**
$f_{C,1}$	22.56	44.03	88.39	0.3508
$f_{C,2}$	23.74	46.62	94.41	0.3311
$f_{C,3}$	22.49	43.86	87.99	0.3521
$f_{C,4}$	22.24	43.32	86.77	0.3566
$f_{C,5}$	21.57	41.83	83.22	0.3689
$f_{C,6}$	23.45	46.00	93.02	0.3358
[min;max]	**[21.57;23.74]**	**[41.83;46.62]**	**[83.22;94.41]**	**[0.3311;0.3689]**

Situation C corresponds to two noisy experiments at two different temperatures.
As shown in **Appendix C: virtual experimental data** (fischer21c-supp.pdf), the region of probable values of (A, Ea) is considerably smaller than in situation B. While the differences between the delay times and $p_{critical}$ are considerably smaller than in situation A and B, the delay times are systematically under-predicted whereas $p_{critical}$ is systematically over-predicted. This could be an artefact of the choice of the six prior distributions and could possibly be avoided by choosing a parametric family of priors instead.

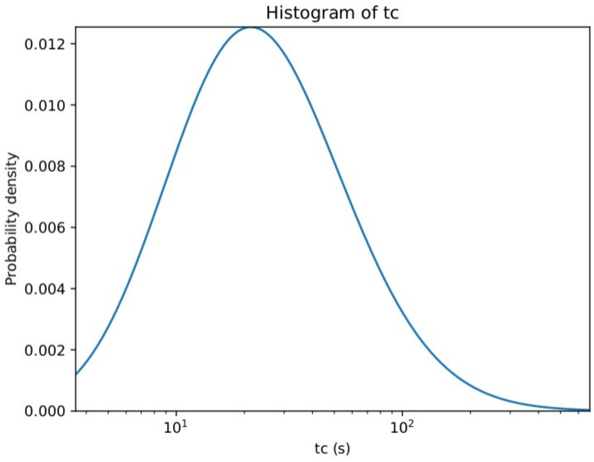
Situation D



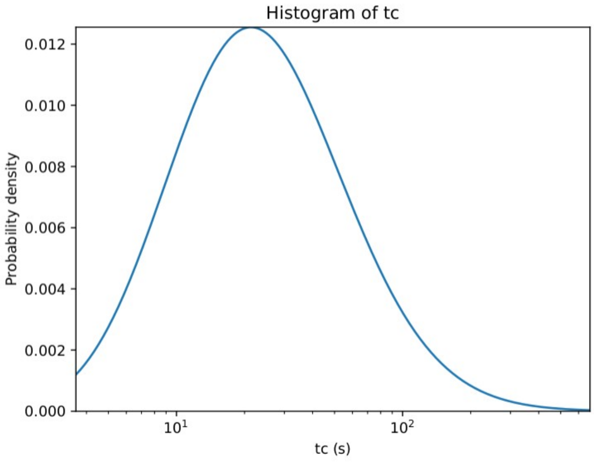
$f_{D,1}$



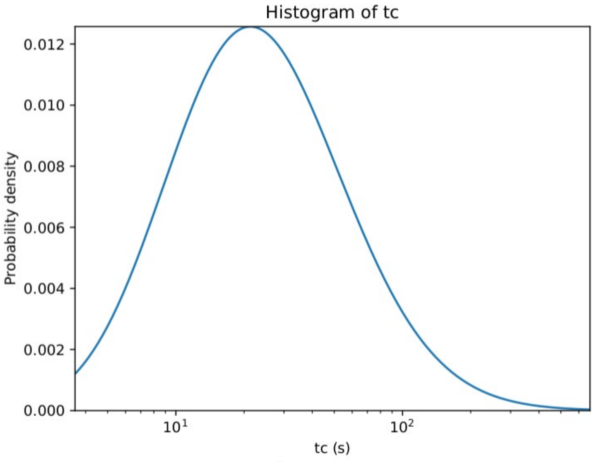
$f_{D,2}$



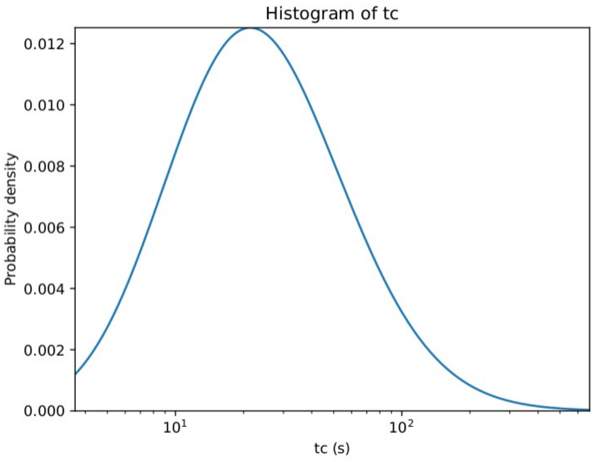
$f_{D,3}$



$f_{D,4}$



$f_{D,5}$



$f_{D,6}$

Posterior	tc_{25}	tc_{50}	tc_{75}	$p_{critical}$
A_0, Ea_0	**28.86**	**55.08**	**108.79**	**0.2634**
$f_{D,1}$	28.55	54.53	107.77	0.2672
$f_{D,2}$	28.61	54.65	108.03	0.2664
$f_{D,3}$	28.54	54.52	107.75	0.2672
$f_{D,4}$	28.53	54.49	107.70	0.2674
$f_{D,5}$	28.48	54.40	107.51	0.2680
$f_{D,6}$	28.60	54.62	107.98	0.2666
[min;max]	**[28.48;28.61]**	**[54.40;54.65]**	**[107.51;108.03]**	**[0.2664;0.2680]**

In that situation, the six posteriors were computed from four experiments at four different temperatures with a low relative standard deviation σ_r = 6%. The quantiles and $p_{critical}$ are almost the same. The very slight under-prediction of the delay times and over-prediction of $p_{critical}$ might stem from the numerical approximations used to compute t_c or from the fact that no parametric family of prior distributions was considered for this study.