ON THE DERIVATION OF POLYURETHANE FOAM KINETIC PARAMETERS USING GENETIC ALGORITHMS

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Abstract

There is a lack of quantification for the kinetic mechanisms of polyurethane-foam thermal-decomposition. This quantification requires the derivation of rate and stoichiometric parameters from experimental data, and poses considerable difficulties due to limitations of classical methods. The objective of this work is to apply the multidimensional optimization technique of Genetic Algorithms to the extraction of the parameters from thermogravimetric experiments. A simple mathematical model of polyurethane-foam decomposition is developed, which accounts for different pyrolysis and oxidation reaction-pathways through Arrhenius-type reaction rates. The model is incorporated into a genetic algorithm to find the kinetic parameters that better reproduce the experimental curves and thus quantify the different reaction mechanisms. The emphasis of the work is on the conditions that pertain to smolder combustion and the results should be applicable in numerical models accounting for heterogeneous surface-reactions of polyurethane foam. Smoldering is a low-temperature, flameless form of combustion propagating inside porous solids. This work is part of the research program being conducted at UC Berkeley and funded by NASA to study smoldering and transition to flaming of porous combustible materials in microgravity and normal-gravity conditions.

1. Polyurethane Kinetics

Thermogravimetric Analysis (TGA) is a testing procedure in which changes in the weight of a solid specimen are recorded as it is heated in a controlled atmosphere. TGA curves provide information regarding the different reactions taking place in the solid material. The experiments of Chao et al. [1] for polyurethane foam are used in this work. The tests in inert atmosphere (100% N_2) are used to study the pyrolysis paths, and in air atmosphere to study the oxidation paths. Experiments at heating rate of 20°C/min show two global pyrolysis reaction-paths and three global oxidative reaction-paths. The temperature range where each reaction takes place depends on the heating rate. The kinetics of polyurethane can be approximated by a few heterogeneous reaction: **pyrolysis and oxidations**. A three-step chemical-reaction scheme for polyurethane foam was proposed by Ohlemiller [2]; foam pyrolysis, foam oxidation and char oxidation, accounting for three solid species; foam, char and residue. However, TGA results suggest that a five-steps mechanism is more appropriate; two foam pyrolysis, foam oxidation and char oxidation. The two pyrolysis paths are associated with the main constituents of polyurethane foam; diisocyanate (α) and polyol (β).

3-reaction Mechanism by Ohlemiller [2]

$$\text{foam} \rightarrow \nu_{c,p}\,\text{Char} + \nu_{g,p}\,\text{Gas}$$
$$\text{foam} + \nu_{O,o}\,O_2 \rightarrow \nu_{c,o}\,\text{Char} + \nu_{g,o}\,\text{Gas}$$
$$\text{Char} + \nu_{O2,c}\,O_2 \rightarrow \nu_{r,c}\,\text{Residue} + \nu_{g,c}\,\text{Gas}$$

New 5-reaction Mechanism

$$\alpha\text{-foam} \rightarrow \nu_{c,p\alpha}\,\text{Char} + \nu_{g,p\alpha}\,\text{Gas}$$
$$\beta\text{-foam} \rightarrow \nu_{c,p\beta}\,\text{Char} + \nu_{g,p\beta}\,\text{Gas}$$
$$\begin{cases} \alpha\text{-foam} + \nu_{O,o}\,O_2 \rightarrow \nu_{c,o}\,\text{Char} + \nu_{g,o}\,\text{Gas} \\ \beta\text{-foam} + \nu_{O,o}\,O_2 \rightarrow \nu_{c,o}\,\text{Char} + \nu_{g,o}\,\text{Gas} \end{cases}$$
$$\text{Char} + \nu_{O2,c}\,O_2 \rightarrow \nu_{r,c}\,\text{Residue} + \nu_{g,c}\,\text{Gas}$$

2. Mathematical Model

A simple mathematical model simulating TGA experiments has been implemented following the kinetic mechanisms outlined above. The model consists on the integration of the solid weight time-change assuming Arrhenius-type reactions rates, and simulating the conditions of temperature and oxygen concentration as those under the thermogravimetric experiments. The weight loss is calculated with a stiff differential solver in Matlab (ODE23S). For any of the two mechanisms studied, the number of parameters to be optimized is on the order of 15, and therefore a multidimensional and robust optimization technique, such as Genetic Algorithms, is needed.

$$\frac{d}{dt}\left(\frac{W}{W_0}\right) = \frac{d}{dt}\left(\frac{W_f}{W_0}\right) + \frac{d}{dt}\left(\frac{W_c}{W_0}\right) + \frac{d}{dt}\left(\frac{W_r}{W_0}\right) = \sum_i (\nu_i - 1)\dot{\omega}_i \qquad \dot{\omega}_i = A_i e^{-\frac{E_i}{RT}} \left(\frac{W_i}{W_0}\right)^{n_i} (y_{O_2})^{n_{oi}}$$

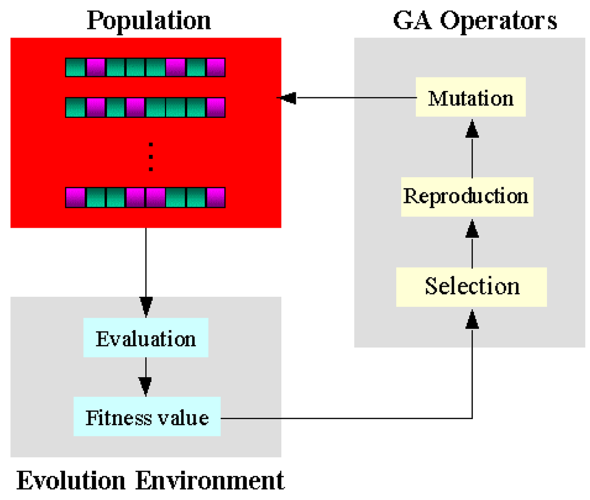
$$\sum_i (\nu_i - 1)\dot{\omega}_i = \begin{cases} \textbf{3-reaction Mechanism: } \frac{d}{dt}\left(\frac{W}{W_0}\right) = (\nu_{c,p} - 1)\dot{\omega}_p + (\nu_{c,o} - 1)\dot{\omega}_o + (\nu_{r,c} - 1)\dot{\omega}_c \\ \textbf{5-reaction Mechanism: } \frac{d}{dt}\left(\frac{W}{W_0}\right) = (\nu_{c,p\alpha} - 1)\dot{\omega}_{p\alpha} + (\nu_{c,p\beta} - 1)\dot{\omega}_{p\beta} + \\ \qquad + (\nu_{c,o} - 1)(\dot{\omega}_{o\alpha} + \dot{\omega}_{o\beta}) + (\nu_{r,c} - 1)\dot{\omega}_c \end{cases}$$

With the conditions:

$$W/W_0 = 1 \text{ and } T = T_0 \text{ for } t = 0 \quad \text{and} \quad \begin{cases} y_{O2} = 0 \text{ (inert atm.) or } y_{O2} = 0.23 \text{ (air atm.)} \\ \frac{dT}{dt} \equiv \text{constant} \end{cases}$$

3. Genetic Algorithms

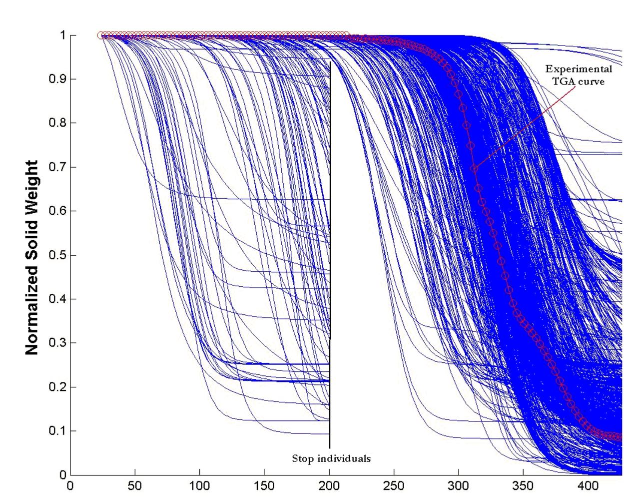
A Genetic Algorithm is a robust and efficient optimization technique imitating the principles of biological adaptation and evolution based upon the mechanics of the Darwinian **survival-of-the-fittest** theory. The procedure is the following; a population of parameter sets undergoes a process of selection such that only those giving the best results (the fittest) of every generation survive. Children of next generation are reproduced from the parameter-set pool of the parents, plus random mutations. The code used is GAOT by Houck et al. [3] for Matlab.



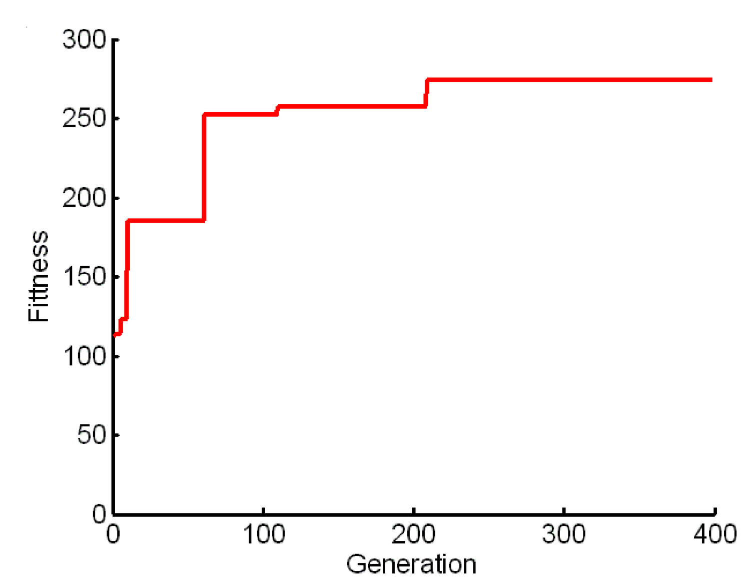
GA Flow Diagram

The fitness function (kind of inverse of the error) used in this work to measure the adaptation of each parameter set is defined as the inverse of the sum of the absolute differences between the numerical solution and the experimental data, for both the weight solution and the time derivative solution:

$$\text{fitness} = 8\left(10^{-5} + \int_{T_0}^{T_f} \left|W_{num} - W_{exp}\right| dT\right)^{-1} + 20\left(10^{-5} + \int_{T_0}^{T_f} \left|\frac{dW_{num}}{dt} - \frac{dW_{exp}}{dt}\right| dT\right)^{-1}$$



Example; All individuals tested in 300 generations



Example; Evolution of the best individual found at each generation

4. Results & Discussion

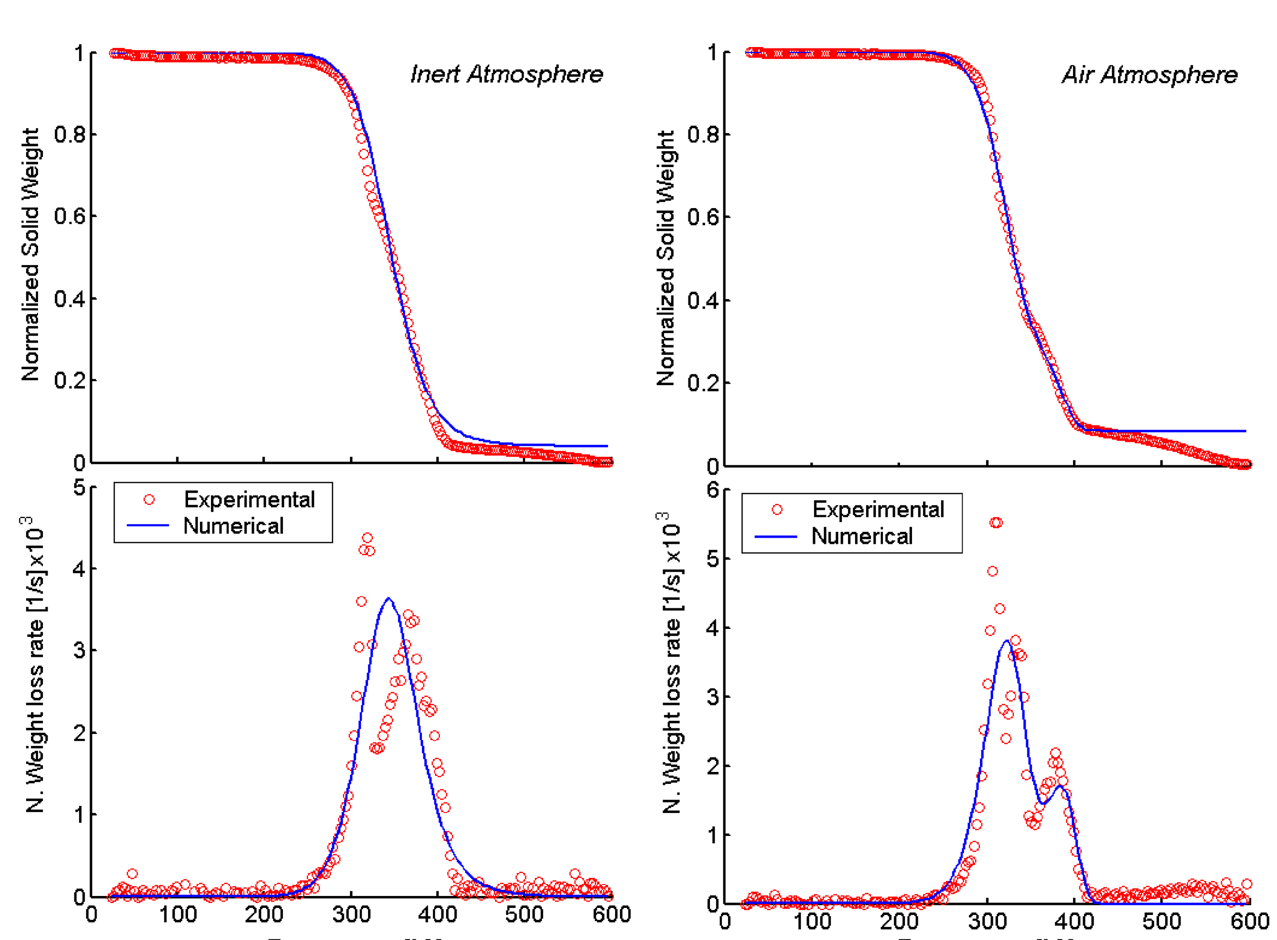
Following the two mechanisms indicated above, the kinetic parameters that best fit the TGA experiments have been derived. The experiment in inert atmosphere (100% N_2) is used to extract the pyrolysis parameters, and in air atmosphere to extract the oxidation parameters.

The **3-reaction mechanism** in the inert atmosphere approximates well the solid weight profile but is not able to capture the two weight loss-rate peaks. In air atmosphere, the curve of weight-loss rate captures only two of the three peaks. These results point out that one global reaction is missing in the mechanism. The **5-reaction mechanism** is able to capture all the peaks in the weight loss-rate curves and approximates properly the solid weight profile, indicating the success of adding another pyrolysis step.

As can be seen for the TGA curve in air atmosphere, none of the mechanisms studied captures the weight loss in the temperature range between 420 and 600°C; this is due to the exclusion of a slow secondary oxidation reaction which should be included.

The heating rate of 20 °C/min has been chosen because it represents better the typical smoldering combustion conditions of polyurethane foam. However, the performance of these kinetic parameters at different heating-rates indicates that they are also valid at least in the range from 5 to 20 °C/min.

3-reaction Mechanism by Ohlemiller [2]



Parameter	Value	
Ap	1.58E+09	1/s
Ep	130.8	kJ/mol
np	1.9	-
$\nu_{c,p}$	0.04	g/g
Ao	2.00E+12	1/s
Eo	155.0	kJ/mol
no	1.1	-
$\nu_{c,o}$	0.41	g/g
Ac	3.78E+13	1/s
Ec	185.0	kJ/mol
nc	1.0	-
$\nu_{r,c}$	0.26	g/g

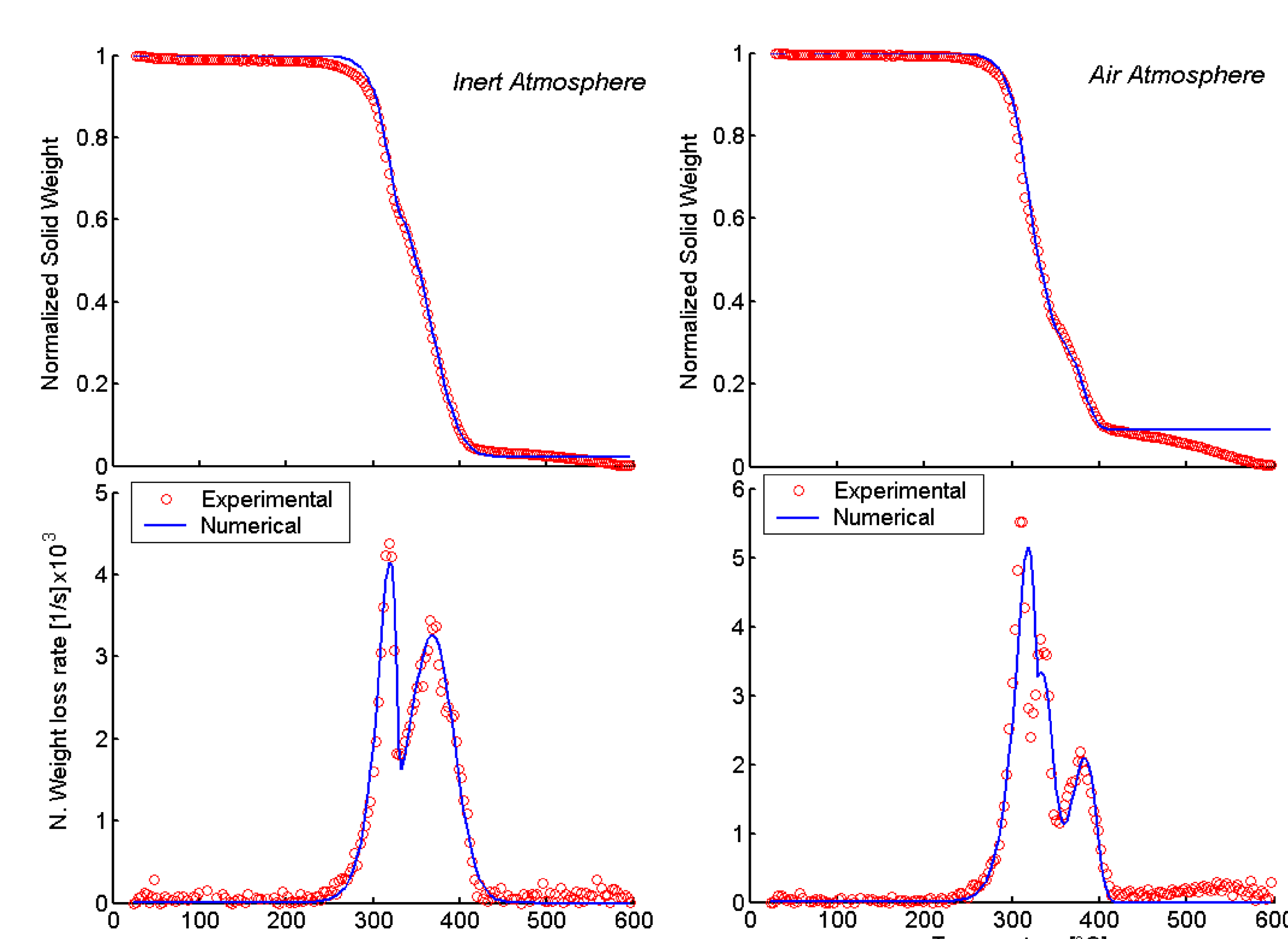
12 Kinetic parameters for the 3-reaction mechanism

Comparison of TGA curves at 20°C/min; Numerical for 3-reactions and Experimental
a) Inert Atmosphere (left), b) Air Atmosphere (right)

New 5-reaction Mechanism

Parameter	Value	
Ap_a	6.90E+16	1/s
Ep_a	211.0	kJ/mol
np_a	0.6	-
$\nu_{c,pa}$	0.00	g/g
w_{0a}	0.28	g/g
Ap_b	2.71E+09	1/s
Ep_b	138.4	kJ/mol
np_b	1.3	-
$\nu_{c,pb}$	0.03	g/g
Ao	9.56E+16	1/s
Eo	209.6	kJ/mol
no	1.0	-
$\nu_{c,o}$	0.50	g/g
Ac	4.68E+17	1/s
Ec	234.7	kJ/mol
nc	1.0	-
$\nu_{r,c}$	0.27	g/g

17 Kinetic Parameters for the 5-reaction mechanism



Comparison of TGA curves at 20°C/min; Numerical for 5-reactions and Experimental
a) Inert Atmosphere (left), b) Air Atmosphere (right)

Conclusions & Future Work

- Genetic Algorithms are a efficient and easy to implemented tool to extract global kinetics from the comparison of a simple mathematical model to experiments.
- Using thermogravimetric experiments [1], the kinetics of polyurethane foam has been quantified, showing that the proposed 5-reaction mechanism gives better results.
- The extracted values for the pre-exponential factor and the activation energy are considerably sensitive to modeling conditions.
- As suggested from TGA experiments, the simplified mechanism will be further completed with the inclusion of secondary oxidation of the residue at high temperature. And the effect of modeling the two pyrolysis paths as consecutive instead of as independent will be studied.
- These new kinetic and stoichiometric parameters are being used in a numerical transient model of smoldering combustion of polyurethane foam, in a similar fashion as done in [4].

References

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4. G. Rein, A. Bar-Ilan, A.C. Fernandez-Pello, J.L. Ellzey, J.L. Torero and D.L. Urban, "Modeling of One-Dimensional Smoldering of Polyurethane in Microgravity Conditions" 30th International Symposium on Combustion, Chicago, July 2004 (this symposium).