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Aziza Chairat, Zhiya Duan, Olivier Fiquet, Carine Ablitzer, Laurent Cassayre, et al.. Modeling of a pyrolysis process for the elimination of epoxy resin from embedded nuclear fuels. *Computer Aided Chemical Engineering*, 2017, 40, pp.343-348. 10.1016/B978-0-444-63965-3.50059-3 . hal-01842285

HAL Id: hal-01842285

<https://hal.science/hal-01842285>

Submitted on 18 Jul 2018

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Official URL: <http://doi.org/10.1016/B978-0-444-63965-3.50059-3>

To cite this version: Chairat, Aziza  and Duan, Zhiya  and Fiquet, Olivier and Ablitzer, Carine and Cassayre, Laurent  and Vergnes, Hugues  and Floquet, Pascal  and Joulia, Xavier 
Modeling of a pyrolysis process for the elimination of epoxy resin from embedded nuclear fuels. (2017) *Computer Aided Chemical Engineering*, 40. 343-348. ISSN 1570-7946

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Modeling of a pyrolysis process for the elimination of epoxy resin from embedded nuclear fuels

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Abstract

This paper presents the modeling of a bench-scale reactor for the pyrolysis of epoxy resin containing nuclear fuel samples. Strict operating conditions must be met to avoid nuclear fuel oxidation and the final hydrogen content in the residual char must be close to zero. By using the finite element method software, COMSOL Multiphysics®, transport phenomena and reaction kinetics can be combined to obtain a representative model of the reactor in terms of the temperature and the concentration distribution of the representative chemical species. The numerical results have been found consistent with the temperature measurements in the reactor. The model is also able to predict the distribution of permanent gases in the reactor over time. The variation in the composition and concentration of the gas near the fuel sample can then be monitored to control the oxygen potential. We have calculated the in-vessel transfers of a representative species of gases, hydrogen. The comparison of simulated and experimental values for hydrogen shows good agreement.

Keywords: pyrolysis, multiphysics modeling, epoxy resin, nuclear fuel

1. Introduction

Metallographic examination is one of the key steps of nuclear fuel characterisation. Epoxy resin is mainly used as the embedding material during metallographic preparation of fuel samples. These samples are generally stored without any treatment following characterisation. Under storage conditions, however, the presence of organic products in contact with highly radioactive materials may generate gases, including hydrogen, due to the radiolysis phenomenon. With the increasing emphasis on safety, the elimination of epoxy resin from spent fuel samples has become indispensable. To satisfy this requirement, a pyrolysis process is currently being developed and a pilot reactor has been built to conduct the relevant experimental studies. Understanding the thermochemical phenomena occurring in the reactor is fundamental to achieve an optimal level of process design and control. Strict operating conditions must be met to avoid fuel oxidation, and the final hydrogen content in the residual char must be close to zero. We have modelled the heat, mass and momentum transfers in the reactor taking into account the pyrolysis kinetic model in order to determine the local conditions, notably the oxygen potential, in the immediate vicinity of the fuel samples.

Non-isothermal thermogravimetric investigations were carried out in a preliminary study. An apparent kinetic model of epoxy resin pyrolysis was obtained from the experimental data (A. Chairat *et al.*, 2015). Qualitative and quantitative analyses, such as μ -GC, tar protocol, solid-phase micro-extraction (SPME) and solid-phase adsorption

(SPA) (M. Israelsson *et al.* 2013), were then used to characterise the products formed during pyrolysis (incondensable gases, H₂O and tar). The formation of various volatile products was modelled based on these measurements, with the reaction scheme presented in Eq. (1), where A_i represents a volatile product formed during pyrolysis (A. Chairat, 2015). The formation of A_i is assumed to be a gas release process during which the species A_i, initially in resin solid, discharges by heating. In Eq. (2), the reaction rate is represented using an Arrhenius form rate constant k as Eq. (3). The reaction yield ξ at time t is written as the ratio of the temporarily released gas quantity w_t versus the final released quantity w_0 . The kinetic parameters of this reaction were determined by a non-linear regression method (A. Chairat, 2015).



$$\frac{d\xi}{dt} = k(1 - \xi)^n \quad (2)$$

$$\text{With } k = k_0 \exp\left(\frac{-E_{act}}{RT}\right) \quad \text{and} \quad \xi = \frac{w_t}{w_0} \quad (3)$$

This is based on the integration of the above-mentioned kinetic models into the transport model of the reactor in COMSOL Multiphysics[®]. COMSOL Multiphysics[®] software is a powerful finite-element method (FEM), partial differential equation (PDE) solution engine (RW. Pryor, 2009). It makes it possible to develop the model taking into account multiple phenomena: heat, mass and momentum transfers and chemical reactions in our case.

2. Reactor description

The reactor is an experimental bench-scale apparatus which has been designed as the pilot unit of the future process. It consists of an indirectly heated reactor operating at ambient atmospheric pressure, which is installed in a furnace able to reach temperatures up to 1200°C. Due to the short distance between the furnace and reactor wall, the heat is conducted through a quasi-stagnant air layer (the inlet and outlet are filled with insulation material) instead of through direct contact.

The pyrolysis reactor is made of two horizontal cylindrical vessels. The vessel in zone 1 (Figure 1) has an internal diameter of 132 mm and a length of 512 mm. The other vessel in zone 2 has an internal diameter of 90 mm and a length of 750 mm. These two zones are connected by a 16 mm internal tube with a length of 32 mm to prevent backflow from zone 2 to zone 1. Zone 2 had been designed for secondary treatment. This operation is not considered in the model for this study.

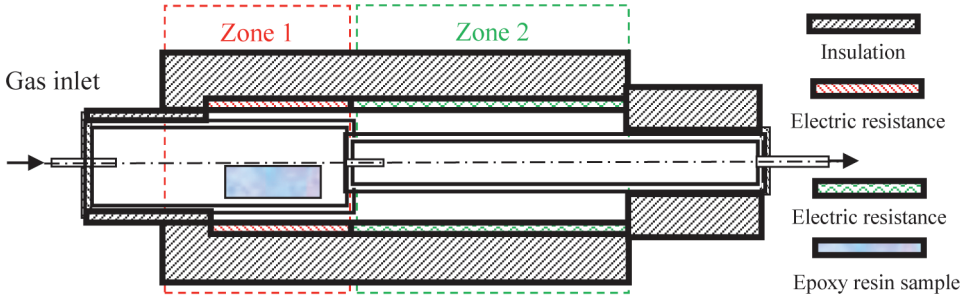


Figure 1: Sketch of the reactor for the thermal treatment of epoxy resin

Before the experiments, the resin sample (20 g cured in a cylinder mounting cup with 24 mm height and a diameter of 33 mm) is placed in a square stainless dish (side length of 83 mm and height of 30 mm) placed on the reactor's inner surface near the bottom side (connection section) of vessel 1. The vessel is then closed by fixing the reactor head (Figure 2) and argon is fed to flush the air out of the reactor. After flushing, heating is provided by two electric resistances encircling the reactor surface of zone 1 and zone 2 with a same program, up to the operating temperature of 650°C. Argon is continuously fed through the inlet tube with an internal diameter of 6 mm to sweep the volatile products formed in the reaction zone to zone 2. At the tail-end of vessel 2, a 16 mm diameter tube is connected to form the reactor outlet.

The data acquisition units consist of thermocouples (type K, chromel-alumel) for the temperature measurements and a μ -GC (gas chromatograph) to follow variations in lighter pyrolysis products such as H_2 , CH_4 , CO , CO_2 , etc. In order to measure the temperature inside the reactor while maintaining a good leaktight level in the reactor, a special reactor head was designed (Figure 2) with 4 channels reserved for sampling and a glovebox-like envelope reaching into the reactor with a length of 400 mm and an internal diameter of 6 mm. A thermocouple has been placed in the envelope to measure the temperature profile along the vessel's axis.

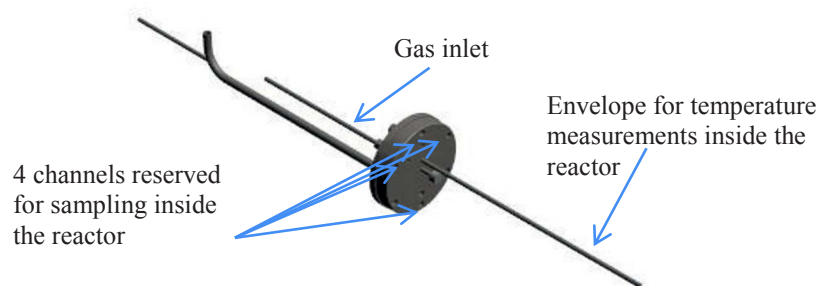


Figure 2: 3D schema of the reactor head

3. Modelling approach

Using COMSOL Multiphysics®, the whole reactor was discretized using a 2D-axisymmetric geometry. Figure 3 shows the reaction zone of the system, highlighting the gas sampling point P_1 where experimental and simulated data were compared. Due to the limits of the current measurement device, positions P_2 , P_3 and P_4 were only investigated by simulation. More sampling points will be taken into account in the follow-up to this work.

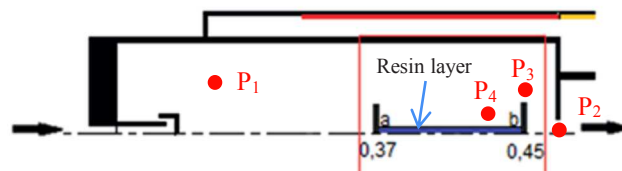


Figure 3: Diagram of zone 1 (reaction zone) with sampling point P_1

The procedure of modeling in COMSOL consists in coupling PDEs from different application fields. The Chemical Reaction Engineering Module of COMSOL

Multiphysics® is appropriate for describing the space and time distribution of pyrolysis products in a reacting system. The Navier-Stokes equations are applied to the fluid flow (argon in our case) modelling for predicting the fluid velocity and its pressure in the sketched reactor geometry with a classical set of boundary conditions. The fluid velocity is specified at the inlet and pressure prescribed at the outlet. A no-slip boundary condition (i.e., the velocity is set to zero) is specified at the walls.

When dealing with the heat transfer, as the initial condition, a uniform temperature (ambient temperature T_{amb}) was assigned to the whole computational domain. A linear temperature change was imposed for the electric resistances according to the heating program. The external walls of the system (insulation material) were assumed to be adiabatic, while the boundaries of the reactor vessels (metal material) were considered conductive and are described by Eq. (4) below. ρ , C_p and k refer to the material's properties, i.e. density, heat capacity and thermal conductivity.

$$\rho^s C_p^s \frac{\partial T}{\partial t} + \nabla \cdot (k^s \nabla T) = 0 \quad (4)$$

In the gas phase - pyrolysis gas and argon, due to the non-null velocity, the convection term is added for describing the heat transfer in fluids (see Eq. (5)). The gas phase model does not include the heats of reactions because this term is negligible (the pyrolysis products are highly diluted in argon).

$$\rho^g C_p^g \frac{\partial T}{\partial t} + \rho^g C_p^g u \cdot \nabla T + \nabla \cdot (k^g \nabla T) = 0 \quad (5)$$

In order to study the changes in chemical species transported by diffusion and convection, we decided to use the 'transport of diluted species model' in COMSOL Multiphysics® (see Eq. (6)). Due to the large flow of argon, the pyrolysis products were considered diluted and mixture properties such as density and viscosity were assumed to correspond to those of inert gas. C_i refers to the concentration of chemical species i and D_i is the diffusion coefficient of this species in the predefined phase (argon).

$$\frac{\partial C_i}{\partial t} + u \cdot \nabla C_i = \nabla \cdot (D_i \nabla C_i) \quad (6)$$

Another assumption concerns the formation kinetics of the pyrolysis products: during pyrolysis, the resin remains as a layer covering the surface of the sample dish. This assumption is based on the observed 'melting' phenomenon of resin under high temperature. Thus, this resin layer seems to be the source surface from which the pyrolysis products leave. It is considered that the changes of resin's size and morphology do not influence the kinetics. As representative of pyrolysis gases, the kinetic parameters of hydrogen are listed in the table below. μ GC measurements were used to determine of these parameters.

Table 1: Kinetic parameters for the formation of hydrogen

Pre-exponential factor k_0	Activation energy E_{act}	Reaction order n
$5.55 \times 10^4 \text{ [s}^{-1}\text{]}$	$1.33 \times 10^5 \text{ [J.mol}^{-1}\text{]}$	1.34 []

4. Simulation results

As mentioned before, the simulation results of the temperature profile in the reactor have been compared with the experimental measurements. The comparison was performed at a stable operating temperature (650°C , $t = 300$ minutes). Figure 4 shows the different axial temperature profiles over the sample dish (r is the distance between the selected axial line and the axis of reactor). The dashed line in the figure represents the experimental points measured in the reactor head's 'envelope' ($r = 20$ mm). The simulation shows good agreement with the measurements. In addition, the radial temperature difference can be observed on the graph due to the fact that heat source was provided by external resistances.

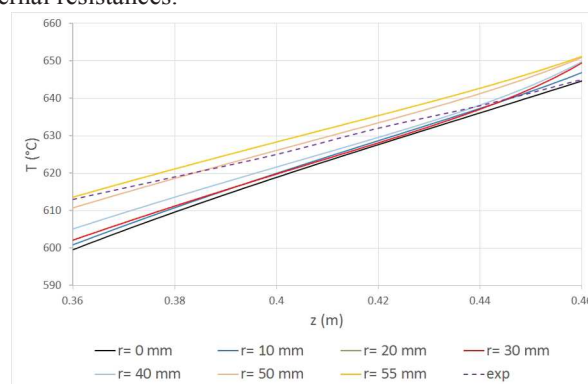


Figure 4: Axial temperature profiles over the sample dish at $t = 300$ min

The variation in the hydrogen concentration at point P_1 was calculated and compared with the μGC measurements (see Figure 5). The simulation results show the same scale of values as the measurements but with a time shift. This shift is probably due to the existence of heat transfer resistance inside the resin.

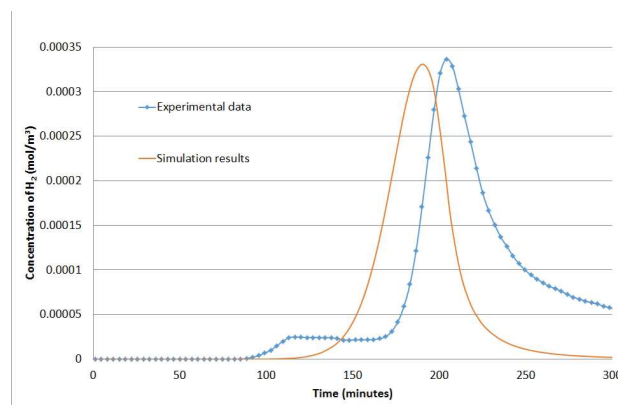


Figure 5: Comparison of measured and calculated hydrogen variations at position P_1

Figure 6 shows the significant variation in the hydrogen concentration at different positions in the reactor. As P_1 is located before the resin sample in the argon flow, the hydrogen concentration here is much less than the three other positions situated above or after the sample. P_2 and P_3 share identical variations in the hydrogen concentration,

while the hydrogen concentration at P₄ is twice that of these two points. These simulation results demonstrate the sensitivity of the sampling positions and the importance of determining the local conditions.

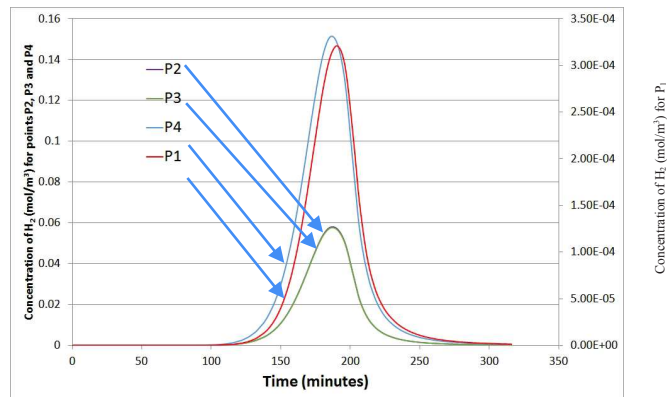


Figure 6: Simulated variations in the hydrogen concentration at different positions: P₁,

5. Conclusion

This paper discusses the development of a resin pyrolysis reactor model for predicting the time and space distribution of the resulting species during the pyrolysis process. The kinetic models generated from thermogravimetric analysis have been integrated into the mass, heat and momentum transport model using the COMSOL Multiphysics® software. Experimental results were used to validate the simulation. The axial temperature profiles in the reactor were found to correspond well with the measurement results. Our assessment of the hydrogen concentration was also compared with the experimental results. Although the results generally tend to be in good agreement, there is a time shift with respect to the formation of hydrogen. Since the proposed model is still being developed, it is not yet possible to assess the impact of resin pyrolysis on nuclear fuels. In order to improve the model's accuracy in predicting the local conditions, further study will make it possible to extend the kinetic model to cover more species known to have a significant impact on nuclear fuels.

6. Acknowledgements

The authors gratefully acknowledge the financial support from the French Alternative Energies and Atomic Energy Commission (CEA).

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