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Application of pyrolysis to remove hydrogen from an organic nuclear waste

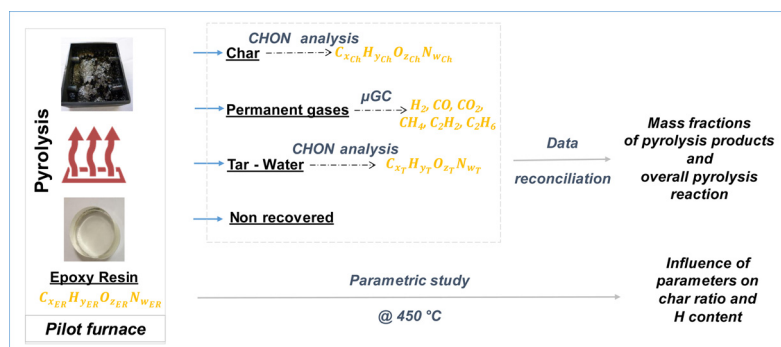
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GRAPHICAL ABSTRACT

Highlights



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ABSTRACT

The work deals with the removal by slow pyrolysis of epoxy resin from samples of spent nuclear fuel embedded in this polymer. Beyond the nuclear field, epoxy resin removal by pyrolysis is a typical issue for the recovery of metals in electronic waste. The main objective is to find the optimal conditions to remove hydrogen in the residual solid waste, in order to avoid hydrogen production by radiolysis during storage and so to prevent any risk of overpressure and explosion. The condensable pyrolysis products (tar-water mixture) and the char were characterised and quantified by elemental analyses, while the permanent gases were quantified by gas chromatography. A data reconciliation method was applied to adjust the values of raw measurements in order to complete the mass balances for both C, H, O and N elements and pyrolysis products. After studying the impact of temperature on the pyrolysis balance, experiments on a pilot furnace were conducted at 450 °C, in the frame of a parametric study of the heating rate, argon gas flow rate, resin mass and plateau time. At fixed temperature, we show that the plateau time is the only significant parameter for minimizing the residual hydrogen content in the char.

- Pyrolysis of epoxy resin in a pilot furnace for the treatment of a

Abbreviations: ch, Char; DOE, Design of Experiments; DOP, Dispersed Oil Particulate; DGEBA, Diglycidyl Ether of Bisphenol A; DTG, Differential thermogravimetric analysis; ER, Epoxy Resin; G, permanent Gas; GC, Gas Chromatography; ND, not detected; T, Tar; TCD, Thermal Conductivity Detector; TETA, triethylene tetramine; TGA, Thermogravimetric Analysis; TW, Tar-Water mixture; W, Water

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Nomenclature

α	stoichiometric coefficient of pyrolysis products
b_i^j	coefficient of parameters of the additive model for the response j
b_0^j	constant of the additive model for the response j
e_i	discrepancies or adjustments between measurements and reconciled data
ε^j	difference between the calculated value and measured value
$g(y_i)$	function of mass balance constraints
i	index of the variable
j	index of the measurement
M_C, M_{Hb}, M_O and M_N	molecular weights of CHON elements (g mol ⁻¹)
$\%M_T, \%M_{Ch}, \%M_G$ and $\%M_W$	mass fraction of pyrolysis products tar, char, gas and water compared with initial mass of epoxy resin
$\%M_{NR}$	mass fraction of non-recovered weight after the pyrolysis
$\%M_{TW+NR}$	mass fraction of tar with adding all of the non-recovered weight
m	number of measurements to be reconciled

n_i	number of the measurements of i^{th} variable
η_H	residual hydrogen ratio
p_i	parameter value
p_1 and p_4	mean normalized values of the heating rate and the plateau time
R^j	response j to be estimated
$\hat{R}^{\%M_{Ch}}$ and \hat{R}^{η_H}	estimated responses of the char ratio and the residual hydrogen ratio (%)
σ_i	standard deviation of a series of measurements for i^{th} variable y_i
x, y, z, w	carbon, hydrogen, oxygen and nitrogen atomic numbers in the constituent
$\bar{x}, \bar{y}, \bar{z}, \bar{w}$	mean values of the CHON atomic numbers in a constituent (raw data)
$\hat{x}, \hat{y}, \hat{z}, \hat{w}$	reconciled data of the CHON atomic numbers in a constituent (reconciled data)
y_i	raw measurement i
\hat{y}_i	estimation of the measurement i meeting the constraints (reconciled data)
y_i^j	j^{th} measurement of i^{th} variable
\bar{y}_i	mean value of all the measurements of i^{th} variable y_i

nuclear waste.

- Focus on the optimal conditions to eliminate hydrogen contained in the solid waste.
- A data reconciliation method is proposed to adjust the values of raw measurements.
- Overall pyrolysis reaction at 450 °C is given based on “model” molecules $C_xH_yO_zN_w$.
- Epoxy resin removal by pyrolysis is an important issue for e-waste valorisation.

1. Introduction

Post-irradiation metallographic examination is a key characterisation step for spent nuclear fuels during a fuel qualification process. Since the 60's, for the purpose of metallographic preparation, nuclear fuel specimens have been embedded in epoxy resins and the resulting samples were stored without any specific treatment after studies. Waste illustrative example is given in supplementary material. However, under long-term storage conditions, organic products in contact with highly radioactive materials induce polymer degradation, which generates gases, including dihydrogen, due to radiolysis (CEA, 2015; Chairat, 2015). For safety considerations, the separation of epoxy resin from spent fuel samples is thus required. The technical solution evaluated in this work consists of thermal degradation of the polymer. The key issues of this treatment are (i) to remove the hydrogen content in the organic part to suppress any further radiolysis hazard in confined storage conditions of the residual solid waste (i.e. spent nuclear fuel + char) after treatment and (ii) to avoid fission products emissions from nuclear fuel through oxidation. This latter issue is related to the properties of the UO_2 phase which composes the ceramic matrix of UOX and MOX fuels. Indeed, the oxidation of UO_2 is a two-step reaction which first leads to the formation of U_3O_7/U_4O_9 , with a slight volume reduction. The second step produces the U_3O_8 phase, which has, in contrast, a density that is 23 % less than that of UO_2 , which corresponds to a 36 % net volume increase and results in the spalling of oxide powder from UO_2 pellets (McEachern and Taylor, 1998). In the case of spent nuclear fuel, the disintegration under oxidative conditions leads to the emission of volatile fission products such as ^{85}Kr . Conversely, in an environment with low oxygen content, the UO_2 matrix is stable (Guéneau et al., 2002), and the oxygen uptake by the UO_{2+x} phase is very slow (Valdivieso et al., 2006). This is why, after a comparative

study of possible chemical, mechanical and thermal processes, slow pyrolysis under argon was selected because it avoids fuel oxidation and ensures safety in the nuclear context. We confirmed, in our previous work (Chairat, 2015), that nuclear fuel UO_2 was only little affected by oxidation during pyrolysis under argon and showed that its presence has no influence on the thermal degradation kinetics of epoxy resin. Thus, in this study, all experimental investigations were carried out with epoxy resin only. In this study, all experimental investigations were carried out with epoxy resin only. A pilot process was built for the experimental studies, including a bench-scale tubular furnace connected to a series of gas filters at its outlet to clean exhaust gases. The polymer system is a commercial epoxy resin called Epofix™. Strict pyrolysis conditions must be met to prevent nuclear fuel oxidation on the one hand, and to minimize the hydrogen content in the residual char on the other hand (Chairat et al., 2017). The latter requirement is quite unusual in studies on pyrolysis processes, and is also the main subject of this article.

Pyrolysis of polymeric material is a growing technology in many industrial fields. The most developed industrial application is the pyrolysis of biomass, which generates useful products such as bio-oil, syngas and bio-char (Demirbaş and Arin, 2002; Wu et al., 2014). More specifically, many on-going research works are focused on the elimination of epoxy resin by pyrolysis as an option in the view of metal recovery from printed circuit board (Gao et al., 2020). This application has strong similarities with our problematic, where the mold resin tightly covers the material (Chen et al., 2018; Gurgul et al., 2018; Liu et al., 2018; Niu et al., 2017).

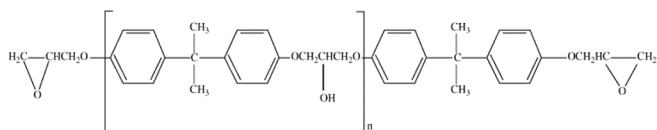
Similarly to any other organic material, the composition of the pyrolysis products (permanent gases, tar and residual char) of epoxy resin strongly depends on the pyrolysis conditions and the initial resin composition. According to previous work carried out on plastic and electronic waste, there is an obvious influence of temperature on the amount and composition of pyrolysis products (Liu et al., 2018; Niu et al., 2017; Ding et al., 2012; Park et al., 2012). It is therefore crucial to understand the thermochemical phenomena occurring in the furnace during the pyrolysis of epoxy resin to optimise the process design, process operating conditions and safety control. The epoxy polymer chains break down into a large variety of smaller molecular fragments made up of numerous chemical species (Beyler and Hirschler, 2002), due to two categories of reactions: chain rearrangement and cleavage reactions (Kuo et al., 2016).

Other studies have shown that several other parameters influence pyrolysis processes. In the present work, the influence of five operating conditions (temperature, heating rate, plateau time, inert gas flow rate and initial mass of resin) on the pyrolysis product distribution has been studied. The experimental data have been analysed on the basis of the total and partial mass balances, as well as on elemental (C,H,O,N) balances from the composition of incondensable gases by gas chromatography, the elemental analysis of epoxy resin, tar and char, and the application of a data reconciliation method. The effects of the parameters have been assessed with respect to the final objective, i.e. minimizing the hydrogen content in the residual char. In addition to the bench-scale experiments, thermogravimetric analysis (TGA) was used to investigate the thermal behaviour of epoxy resin, with similar characterisation procedures.

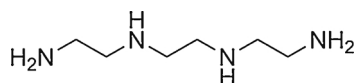
2. Materials and methods

2.1. Epoxy resin

The epoxy resin investigated in this study is the commercial Epofix™ kit distributed by Struers S.A.S. This epoxy resin is obtained by reticulating the bisphenol-A-diglycidylether (DGEBA) polymer



and the triethylenetetramine (TETA) curing agent.



The recommended mixing ratio of 25 parts (weight) of resin for 3 parts of hardener was used to produce 1 kg of epoxy resin. After mixing with an electric stirrer in a 2-litre vessel for about 10 min, the mixture was poured into small cylindrical moulds of different sizes in order to make samples from 10 g to 30 g each.

2.2. Experimental furnace and pyrolysis protocols

2.2.1. Pilot-scale experiments

The pilot unit consisted of a gastight horizontal furnace (supplied by Nabertherm, Lilienthal, Germany) whose outlet was connected to a series of filters for exhaust gas cleaning. Gases were analysed with an online micro-gas chromatograph analyser (μ GC, see Section 2.2.4). The furnace was equipped with two horizontal consecutive-connected cylinders operating at low pressure. The zone 1 (Fig. 1) had an internal diameter of 132 mm and a length of 512 mm. The zone 2 was originally designed for an oxidising post-combustion gas treatment, which was not implemented in this study. These two zones were connected by a 16

mm internal tube with a length of 32 mm.

For each experiment, the resin sample was placed in a square stainless steel dish and placed in furnace zone 1. The pyrolysis treatment consisted of three heating steps: 1) ramp-up (various heating rates) from ambient to the final pyrolysis temperature, 2) holding of the maximum temperature for a plateau time and 3) cool-down to ambient temperature.

After initial gas flushing, the argon carrier gas was supplied continuously to maintain an inert atmosphere in the furnace and sweep the volatile products into the filters through a pipeline heated at 300 °C. Four filtering devices mounted in series (Fig. 1) trapped tar and water while the incondensable gases (H_2 , CO, CO_2 , CH_4 , etc.) were characterised by μ GC.

The total amount of tar-water mixture was quantified by weighing the different removable filters before and after pyrolysis with a laboratory balance (precision 0.01 g, KERN, Germany). The tar was then sampled from the different filters for analysis. The square dish was carefully retrieved from the furnace and weighed to determine the mass of residual char. The residual char was collected, ground by hand in a mortar, and sampled for elemental analysis. After each pyrolysis experiment, the whole experimental set-up was cleaned by an oxidising thermal treatment (air flushing at 800 °C for 2 h).

2.2.2. Thermogravimetric experiments

Thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out using a thermal gravimetric analyser (LABSYS evo TGA 1150, SETARAM Instruments, France). Samples of approximately 100 mg were placed in an alumina crucible and operated under high-purity argon (ALPHAGAZ™2 Argon by Air Liquide) with a flow rate of 100 mL min^{-1} . For each run, a given heating rate is applied up to a target temperature, followed by a plateau. Each TGA experiment was repeated twice under identical conditions.

2.2.3. Elemental analysis

Elemental analysis was carried out on the epoxy resin, the residual char and the tar samples with an organic elemental analyser (FlashEA® 1112, Thermo Finnigan, USA). The minimal sample mass was 10 mg. The carbon (C), hydrogen (H) and nitrogen (N) contents were determined together while the oxygen (O) content was measured choosing another procedure with the same kind of equipment (Elemental Analyse, 2020). Each elemental analysis CHON was performed at least twice from the same sample. The mean value of the two measurements for the same material was used as the elemental composition.

The measurements of the epoxy sample showed that 98.9 wt% of the resin was made of the 4 basic elements (C - 70.1 wt%, H - 8.4 wt%, O - 16.5 wt% and N - 3.9 wt%) and can be represented as $C_{37.7}H_{53.8}O_{6.7}N_{1.8}$.

The tar composition from each pyrolysis experiment was calculated from the weighted averages of the different tar samples.

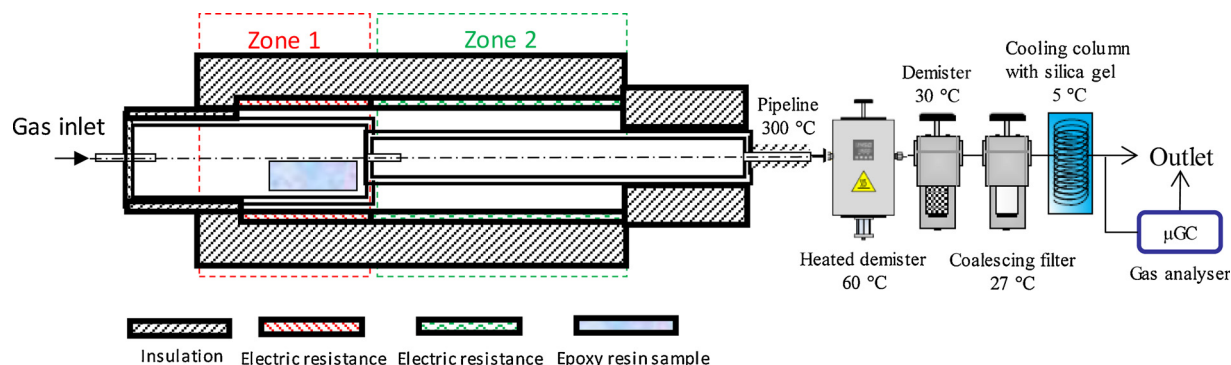


Fig. 1. Pilot device for the thermal treatment of the epoxy resin.

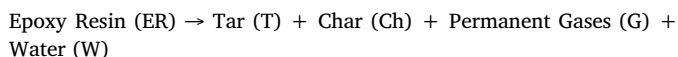
2.2.4. Gas analysis by GC-TCD

For both the pilot and TGA experiments, the output gas composition was determined by a μ GC equipment (model R3000, SRA Instruments, France). The equipment was continuously flushed with high-purity argon. Two separating columns, A (molecular sieve 5 Å) and B (Poraplot Q), provided a time resolution analysis in less than 180 s. A micro thermal conductivity detector (μ TCD) detected gas composition with a response time of 5 ms. It was calibrated in time and pic area by running each certified gas concentrations of H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, and C₃H₈ in pure argon. Calibration curves were then generated by plotting the responses against the reference gas concentrations. No signal corresponding to C₂H₄ and C₃H₈ was detected during any of the runs. The concentrations of the other gases (H₂, CO, CO₂, CH₄, C₂H₂, and C₂H₆) were determined by the integration of corresponding chromatography peaks areas.

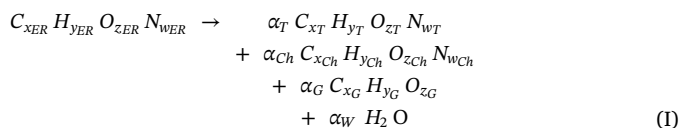
During pyrolysis, the flow rate of argon was controlled and measured by a mass gas flowmeter (SLA5800 series, Brooks Instruments, USA). The volume of the gases produced by pyrolysis, i.e. less than 3.10⁻³ Nm³, was negligible compared with the total amount of argon flushed into the system (i.e. 1.4 to 4.8 Nm³ depending on the flow rate).

2.3. Data processing and reconciliation

For the purpose of data processing and reconciliation, a reaction pathway needs to be chosen to formulate the mass balances of the products (tar, char, gas and water). According to the kinetic study of the thermal degradation of epoxy resin (Chairat et al., 2015), the following single global apparent reaction was considered:



The epoxy resin (ER) and the chemically complex products generated during pyrolysis, i.e. tar (T), char (Ch) and permanent gases (G), are represented by 'model' molecules of the formula C_xH_yO_zN_w, except for permanent gases (formula C_xH_yO_z). Indeed no nitrogen was attributed to the permanent gas composition because nitrogen-containing gases could not be detected. Therefore, the global pyrolysis reaction can be described with the following chemical equation:



with, for each reactant and product: x_i the number of carbon atoms in the pseudo-component i ; y_i the number of hydrogen atoms in i ; z_i the number of oxygen atoms in i ; w_i the number of nitrogen atoms in i ; α_i the stoichiometric coefficient of pyrolysis product i ; $i = T, Ch, G$ and W .

Direct analysis of the raw data collected from the furnace experiments could lead to erroneous interpretations. This is because the overall mass balance based on the recovered mass of all products and the initial mass of epoxy resin showed a discrepancy of about 15 wt%. This noticeable difference can mainly be attributed to tar deposition on the furnace walls and pipes of the experimental device. It was thus decided to attribute all the missing mass to the tar. The mass balances for hydrogen and oxygen did not match up either due to the inaccurate quantification of the water content in the exhaust gases. The presence of water was detected after the filtration unit by the μ GC but it could not be quantified.

These considerations led us to implement a data reconciliation method (do Valle et al., 2018), with the aim of adjusting the measured data according to their uncertainty and estimating the unmeasured physical data, i.e. the stoichiometric coefficients α_i of the global pyrolysis reaction, including the amount of water. The reconciled data proved to be consistent with the process balances imposed in the problem formulation. The data reconciliation procedure is explained in

detail in supplementary material.

2.4. Experiments

2.4.1. TGA experiments

The samples of epoxy resin were treated with heating rates of 1 °C min⁻¹ and 5 °C min⁻¹ from room temperature up to the pyrolysis temperature of 200 °C, 250 °C, 325 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C or 800 °C. The ramp is followed by a plateau from 2 h to 10 h.

2.4.2. Design of experiments (DOE) on pilot scale

The pilot-scale experiments carried out at 450 °C were organized according to a DOE method. These experiments were conducted with a 2-level fractional factorial experimental design to study the influence of the 4 process parameters: heating rate [3–10 °C min⁻¹], argon flow rate [3–10 L min⁻¹], resin mass [10–30 g] and plateau time [0.5–2 h]. This screening design made it possible to identify the factors having the greatest impact on the responses. It consisted of an 8 runs (2⁴⁻¹) and 3 repeated experiments in conditions at the central point, used to calculate the standard deviations σ_i on the measured variables.

An additive model with a first-degree polynomial was used to describe the relationship between the process parameters (factors) and the responses to be estimated (Lundstedt et al., 1998).

$$R^j = b_0^j + \sum_i b_i^j p_i + \varepsilon^j \quad (1)$$

with R^j : experimental response j ; b_i^j : coefficient of parameter i ; b_0^j : constant of the model; p_i : i^{th} parameter value; ε^j : residue which represents the difference between the calculated value and measured value of the response j .

A multi-linear regression was performed to estimate the coefficient b_i^j of the model, i.e. the impact of the corresponding parameter i on the response j . The overall validity of the linear model was then checked by the F -test with regards to experimental variance. Furthermore, the significance of each parameter was assessed individually by the t -test.

The selected responses R^j were the char ratio % M_{Ch} and the residual hydrogen ratio η_H as calculated by Eq. (2):

$$\eta_H = \frac{\alpha_{Ch} y_{Ch}}{y_{ER}} \quad (2)$$

with the aim of minimizing the hydrogen content in the residual char. These two indicators are extremely important in assessing the process performance.

3. Results and discussion

3.1. Effects of the pyrolysis temperature on the char ratio and residual hydrogen content

Char ratios obtained from the pilot and the TGA experiments at different pyrolysis temperatures are compared in Fig. 2. Apart from the DOE performed at 450 °C, the results of experiments performed at the same pyrolysis temperature are represented by their mean values, because the standard deviation of char ratios are less than 0.3 % (DOE experiments at 450 °C).

The global trend, valid for both TGA and pilot experiments, is that the char ratio decreases in the 300 °C–500 °C temperature range. According to the TGA study performed in our previous work (Chairat et al., 2015) on the Epofix™ resin at 660 °C, most weight loss occurs in this temperature range; below 500 °C, the epoxy resin is only partially pyrolysed. Above 500 °C for TGA and 650 °C for the pilot-scale furnace experiments, the influence of temperature is of less importance: a char ratio of about 10 wt% was obtained for both types of experiments. For the pyrolysis of Epofix™ at 660 °C with a heating rate of 3 °C min⁻¹ and a plateau time of 2 h in a TGA device, Chairat et al. (Chairat et al.,

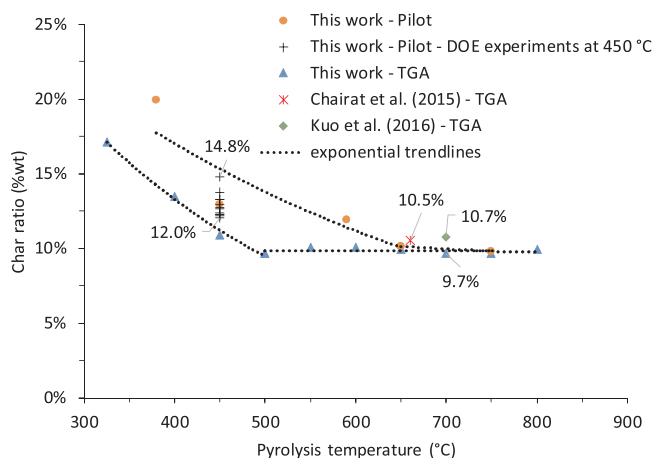


Fig. 2. Influence of the pyrolysis temperature on the char ratio (raw data from the pilot and TGA experiments).

2015) obtained a final char ratio of 10.5 wt%. Based on the pyrolysis of DGEBA epoxy resin at 700 °C, the TGA measurements of Kuo et al. (Kuo et al. (2016)) show a similar char ratio. Fig. 2 also clearly illustrates the difference in pyrolysis kinetics between the pilot and TGA scales. Up to 650 °C, the char ratios from TGA were systematically lower. This can be attributed to a more efficient heat and mass transfer within smaller size samples (mg in TGA vs. g in the furnace) and a more accurate temperature control in the TGA device. The initial size of particles is often considered an important parameter that has an effect on the quantity and reactivity of solid residue (Demirbas, 2004; Zanzi et al., 1996). In addition, the solid resin undergoes a glassy transition at temperature around 110–125 °C. Therefore, the total resin mass to be processed is a more relevant parameter than other variables related to the geometry of the original material. Finally, for pilot experiments, slower tar evacuation results in significant residence times for all primary decomposition products in the pyrolysis matrix. For low-temperature pyrolysis, this phenomenon may lead to repolymerization and higher residue rates (Ahuja et al., 1996).

Fig. 3 shows the residual hydrogen ratio as a function of the temperature, measured by TGA and in the pilot furnace. The standard deviations of residual hydrogen ratios are less than 0.4 % (DOE experiments at 450 °C). In a similar way to the char ratio, the residual hydrogen ratio decreases with temperature; the TGA experiments produce lower residual hydrogen ratios below 650 °C. However, unlike the char ratio, the residual hydrogen ratios for both the TGA and pilot experiments continue to decrease above 650 °C. The decrease is about one order of magnitude between 300 °C and 800 °C, and the hydrogen ratio reaches a value as low as 1 wt% at 800 °C. The weight of released hydrogen from char is so small above 650 °C that the mass loss of char is not noticeable in the data shown in Fig. 2.

Our results are in agreement with previous results reported for the pyrolysis of woods and coals as demonstrated by Della Rocca et al. (Della Rocca et al. (1997)). As detailed by Demirbas (Demirbas (2004)), hydrogen content losses correspond to the scission of weaker bonds within the char at higher temperatures. The dehydrogenation reaction, where hydrogen is stripped from aromatic nuclei, could also take place above 600 °C according to Bishop and Smith (Bishop and Smith (1970)).

Fig. 4(a) shows the residual hydrogen ratio (η_H) versus the char ratio ($\%M_{Ch}$) for all experiments, including TGA results for low-temperature pyrolysis at 200 °C and 250 °C where both η_H and $\%M_{Ch}$ remain high. Standard deviations less than 0.3 % (char ratios) and 0.4 % (residual hydrogen ratios) are observed for each experimental points. The resulting overall linear correlation indicates an overall hydrogen consumption concomitant to the volatilisation of the resin. Comparison between the linear correlation and the line of equality (which

corresponds to the congruent volatilisation of H from the resin) shows that the release of hydrogen is slightly higher than the mass loss of char, and this characteristic amplifies as the pyrolysis progresses. This means that hydrogen element volatilizes to a slightly higher extent than the rest of the elements composing the resin.

Fig. 4(b) focuses on the experiments carried out at temperatures above 300 °C. It illustrates that minimizing the residual amount of char alone is insufficient to minimize the residual hydrogen content in the solid residue despite the general correlation between η_H and $\%M_{Ch}$. As an example, the residual hydrogen ratio decreases from 3 to 1 wt% for the minimal char ratios of about 10 wt%.

In Fig. 2 to Fig. 4, the large dispersion in the ratios at 450 °C corresponds to the set of pilot experiments conducted with the DOE, taking into account various parameters. The choice of specifically studying the operating temperature of 450 °C was driven by the acceptable reduction of both the char and hydrogen ratios obtained at this temperature, combined with our technical and safety constraints that limit the maximal operating temperature of the process.

3.2. Analysis of data from central-point experiments at 450 °C

Table 1–3 show the raw data for the three repeated pilot experiments at 450 °C with a heating rate of 6.5 °C min⁻¹, an argon flow rate of 6.5 L min⁻¹, a resin mass of 20 g and plateau time of 1.25 h.

In Table 1, $\%M_{NR}$ represents the missing mass fraction of non-recovered by-products during pyrolysis, which was mainly attributed to tar deposited in the experimental device. For this reason, the values of $\%M_{NR}$ and $\%M_{TW}$ were assigned to the cumulative variable $\%M_{TW+NR}$. The permanent gas fraction $\%M_G$ represents the cumulative gas mixture whose composition is detailed in Table 2. All missing masses of permanent gaseous species (i.e. not detected by our gas chromatography equipment) were also attributed to $\%M_{NR}$. It includes at least N-containing molecules such as NO and NH₃. In the following data processing steps, $\%M_{Ch}$, $\%M_G$, and $\%M_{TW+NR}$ are the mass fractions to be recalculated by the reconciliation procedure.

The initial epoxy sample mass was measured with an accuracy of at least one order of magnitude lower than the other data, so we assumed $\sigma_{ER} = 0$. All standard deviations were used in the data reconciliation procedure.

Table 3 presents the atomic numbers of each ‘model’ molecule. For epoxy resin (ER), tar (T) and char (Ch), the atomic numbers correspond to the mole fractions based on the CHON elemental analysis. The molecular formula of permanent gas (G) was obtained from the volume fractions (Table 2). In order to show the carbon distribution in the main gaseous molecules such as CO, CO₂ and CH₄, the atomic numbers of permanent gas were normalized to the form of C₁H_yO_z.

Comparing the raw data (\bar{x} , \bar{y} , \bar{z} , \bar{w}) and reconciled data (\hat{x} , \hat{y} , \hat{z} , \hat{w}) in Table 3 of pyrolysis product compositions, as well as

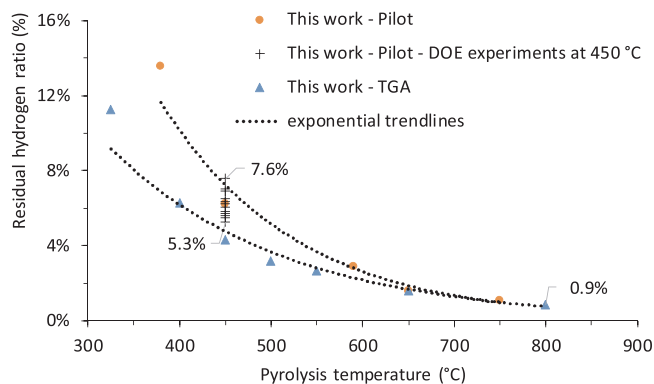


Fig. 3. Influence of the pyrolysis temperature on the residual hydrogen ratio (raw data from the pilot and TGA experiments).

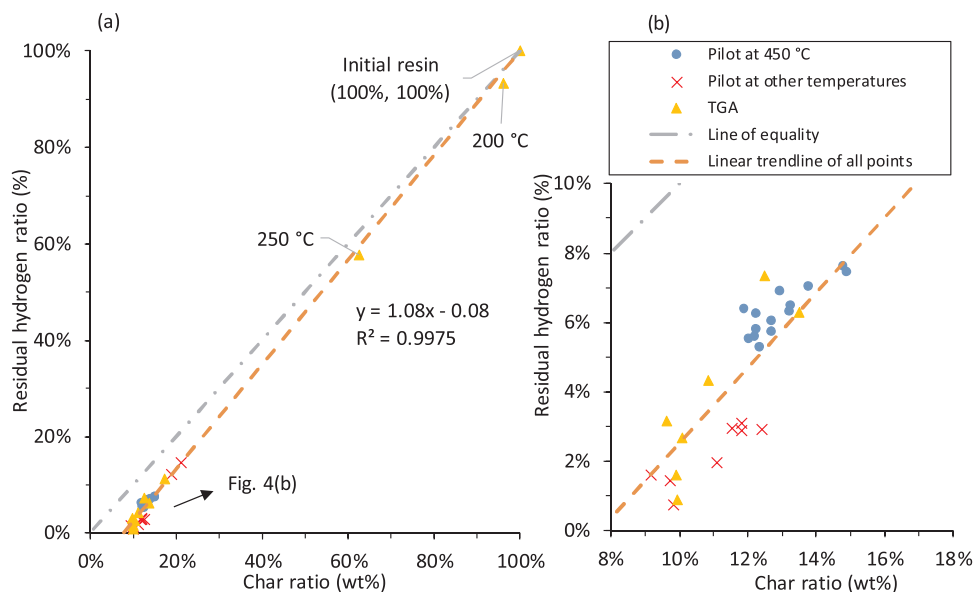


Fig. 4. Correlation between η_H and $\%M_{Ch}$ for TGA and pilot experiments. (a): temperatures between 200 °C and 800 °C (b): focus on temperatures above 300 °C.

Table 1

Mean values (raw data) and standard deviations of pyrolysis product distributions of 3 repeated experiments at 450 °C with central-point conditions.

Repeated Exp	$\%M_{Ch}$	$\%M_G$	$\%M_{TW}$	$\%M_{NR}$	$\%M_{TW+NR}$
Mean value \bar{y} (%)	12.9	2.7	69.5	14.9	84.4
Standard deviation σ (%)	0.3	0.5	1.9	2.0	0.6

Table 2

Mean volume fractions (raw data) of analysed gas products by μ GC based on 3 repeated experiments at 450 °C with central-point conditions (ND: not detected).

Gas products	H ₂	CO	CO ₂	CH ₄	C ₂ H ₂	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈
Volume fraction (%)	11.9	12.9	37.2	17.5	7.8	12.7	ND	ND
Standard deviation σ (%)	0.3	0.4	4.4	4.3	0.4	0.2	ND	ND

the epoxy resin, the discrepancies are within the 95 % confidence interval. Reconciled data shows that the tar composition is close to the initial epoxy resin with slightly more C and H contents, and less O and N. This is in accordance with the release of some water and oxidised products.

Fig. 5 illustrates the comparison between raw data and reconciled data for the distribution of pyrolysis products. As already mentioned, the non-recovered mass (14.90 wt%) was attributed to the tar-water. Thus, the reconciled tar-water mass distribution (84.56 wt%) includes the weights of recovered tar and water and the non-recovered pyrolysis products. Through the mass balance calculation with reconciled data, the mass distribution was 5.82 wt% for water and 78.74 wt% for tar.

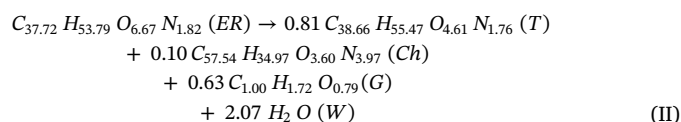
Table 3

Comparison between the measurement means (\bar{x} , \bar{y} , \bar{z} , \bar{w}) and reconciled data (\hat{x} , \hat{y} , \hat{z} , \hat{w}) for CHON elemental analysis of 3 repeated pilot experiments at 450 °C with central-point conditions, reconciliation applied with standard deviations σ . *: values of σ modified to validate the data reconciliation.

Atomic number	Carbon			Hydrogen			Oxygen			Nitrogen		
	\bar{x}	σ	\hat{x}	\bar{y}	σ	\hat{y}	\bar{z}	σ	\hat{z}	\bar{w}	σ	\hat{w}
ER	37.72	0.04	37.72	53.79	0.04	53.79	6.67	0.01	6.67	1.82	0.01	1.82
T	39.39	0.73*	38.66	53.65	1.29*	55.47	5.28	0.56*	4.61	1.67	0.24*	1.76
Ch	57.71	1.35	57.54	34.72	1.35	34.97	3.60	0.04	3.60	3.97	0.06	3.97
G	1.00	0.03	1.00	1.71	0.12	1.72	0.80	0.10	0.79	-	-	-

The raw data adjustments for char and gas were very small but sufficient to ensure mass balance closure on the elements C, H, O and N. Their calculated mass distributions are: 12.84 wt% for residual char and 2.60 wt% for permanent gas.

Based on the reconciled data, the overall pyrolysis reaction at 450 °C can be written with the stoichiometric coefficients provided in Schema II.



To give further chemical meaning to the stoichiometry, the chemical formula of epoxy resin has been normalized with respect to the carbon number in Epofix™'s theoretical formula $C_{16.65} H_{21.32} O_{2.94} N_{0.82}$. The formula for tar can be therefore written as $C_{17.07} H_{24.49} O_{2.04} N_{0.78}$, which leads to a possible mixing ratio for the two main constituents of tar detected by TD-GC/MS: 0.5 part by mole of dodecanol ($C_{12}H_{26}O$) and 2 parts by mole of phenol (C_6H_6O). This high phenol content in tar is in accordance with the investigation of bisphenol A pyrolysis by Gao et al. (Gao et al. (2020)). They concluded that all pathways led to the formation of phenol. Compared with the epoxy resin, the formula for residual char has a much higher C/H (0.70 in resin vs 1.64 in char) and C/O (5.66 in resin vs 15.97 in char) ratio, which is in agreement with the charring reaction that involves removing hydrogen and oxygen from the solid material during pyrolysis. The permanent gases are expressed as a set of molecules in Schema III, with the coefficients determined from the average gas concentrations (Table 2). CO₂ is the major gas, while the other molecules have rather similar concentrations.

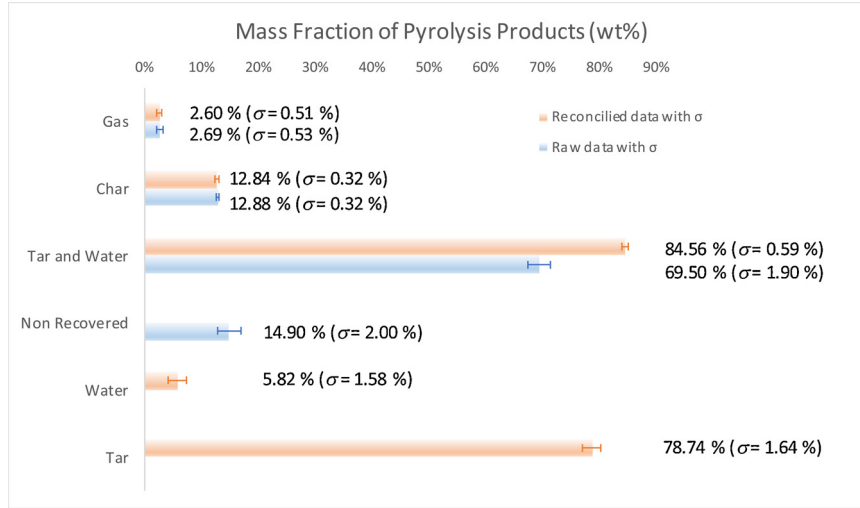
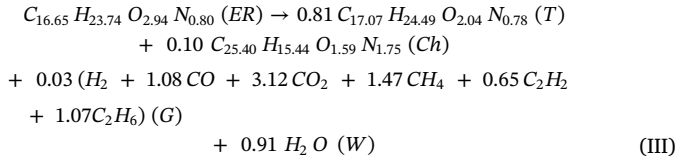


Fig. 5. Comparison between the measurement means and reconciled data for the mass distributions of 3 repeated pilot experiments at 450 °C with central-point conditions.



3.3. Effects of parameters on the char ratio and residual hydrogen ratio

Based on the reconciled data obtained from all 11 pilot experiments performed at 450 °C, the effect of the four parameters can be assessed on the basis of the regression coefficients. Fig. 6 represents the value of these coefficients with regard to the two selected responses: the char ratio and the residual hydrogen ratio. The constant coefficients are equal to 12.82 wt% and 6.36 wt% for char ratio and residual hydrogen ratio respectively. The overall F-tests for these two models are both significant (p-value < 0.05). This suggests that they depend on at least one of the parameters. Furthermore, the individual t-tests on each regression coefficient indicate that the significant parameters for the char ratio are the plateau time and the heating rate. For the residual hydrogen ratio, only the plateau time is statistically significant (p-value < 0.05).

As shown in Fig. 6, the plateau time is the predominant parameter and it has a negative effect ($b_i^{\%M_{Ch}} = -0.59$ and $b_i^{\eta_H} = -0.59$) on both responses. It confirms that, at constant temperature, an increase in the reaction time reduces the amount of char and the final hydrogen content. At 450 °C, the volatilisation reaction during which the amount of solid material decreases dominates the charring reaction (Demirbas, 2004). This fact, therefore, results in the reduction of the char ratio.

The heating rate is another significant parameter for the char ratio and it has also a negative effect ($b_i^{\%M_{Ch}} = -0.49$). Even if the effect of the plateau time is similar for both indicators, the residual amount of hydrogen is much less affected by the heating rate ($b_i^{\eta_H} = -0.22$) than the char amount. In the case of biomass, rapid pyrolysis is preferred for increasing the production of volatile products while slow pyrolysis is used to produce bio-char as demonstrated by Al Arni (Al Arni (2018)) and Williams and Besler (Williams and Besler (1996)).

In our set of reconciled data, the argon flow rate was not significant according to the t-tests. This is in agreement with the results of Niu et al. (Niu et al. (2017)) that the argon flow rate had little influence on the char, while markedly affected the yield of gas and tar.

According to the statistical hypothesis tests, the influence of the epoxy resin mass is neither significant on the char ratio nor on the residual hydrogen ratio within the DOE range.

Neglecting the non-significant parameters, the derived models for representing the relations between the parameters (normalized to -1, 0 and 1) and responses can be written as in Eq. (3) and Eq. (4) for $\%M_{Ch}$ and η_H respectively.

$$\hat{R}^{\%M_{Ch}} = -0.49p_1 - 0.59p_4 + 12.82 \quad (3)$$

$$\hat{R}^{\eta_H} = -0.59p_4 + 6.36 \quad (4)$$

where $\hat{R}^{\%M_{Ch}}$ and \hat{R}^{η_H} are the estimated responses of the char ratio and the residual hydrogen ratio (%); p_1 and p_4 represent the mean-normalized values of the heating rate and the plateau time.

4. Conclusion

Within the scope of developing a process to treat spent nuclear fuel samples embedded in epoxy polymer, the pyrolysis of a commercial epoxy resin (Epofix™) was studied using both a pilot furnace and a laboratory TGA device. The influence of five parameters was considered with the objective of optimising the process to minimize the final hydrogen content in pyrolysis residue.

As already largely described in the literature, the pyrolysis temperature is the most influent parameter on the amount of residual char,

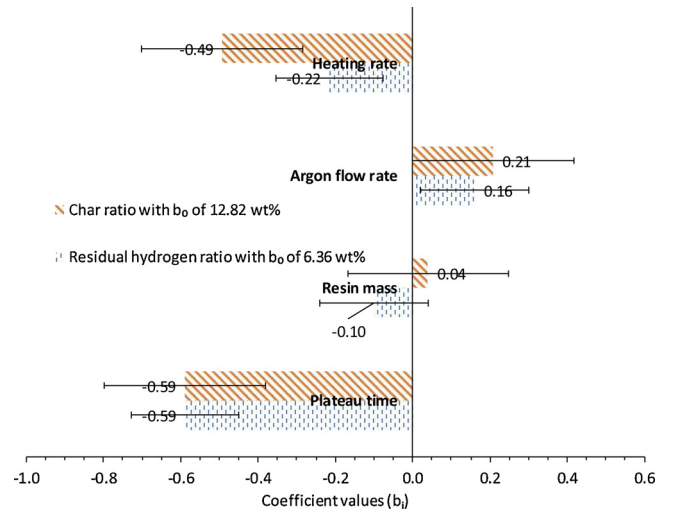


Fig. 6. Influence of parameters on the char ratio and residual hydrogen ratio for the pyrolysis experiments at 450 °C.

with a minimum threshold of about 500 °C to reach a constant value of 10 wt% of char (100 wt% for initial mass of resin). In the present work, we have shown that the hydrogen content within the char continues to decrease with the temperature at least until 800 °C.

Due to process operation constraints linked with existing nuclear materials and facilities, the maximal temperature in the future industrial process has been limited at 450 °C. The temperature was thus fixed at 450 °C for the parametric study of four other parameters, namely the heating rate, argon flow rate, resin mass and plateau time. Based on the implementation of a data reconciliation method, the raw measurements (i.e. weighing and CHON analyses of tar and char, μ GC analyses of incondensable gases) obtained from a 2-level fractional factorial experimental design were adjusted to satisfy the mass balances of C-H-O-N elements and obtain the mass fractions of tar, char, gas and water. The resulting distribution of the pyrolysis products at 450 °C stands as:

- 78.74 wt% of tar, with an average molar composition close to the initial resin composition and the three main components detected by TD-GC/MS were phenol, 4-isopropylphénol and 1-dodecanol;
- 2.60 wt% of incondensable gases, the dominant molecule being CO₂ (37 % in volume);
- 12.84 wt% of residual char, with a C/H and C/O ratio much higher than in the initial resin;
- 5.82 wt% of water, resulting from the data analysis and reconciliation method since direct measurement was not achievable.

At the pyrolysis temperature of 450 °C, the two predominant parameters for the char ratio are the plateau time and the heating rate, while the influence of the argon flow rate and the initial resin mass are negligible. For the residual hydrogen ratio, only the plateau time has statistical significance.

Beyond our specific application in the nuclear field, removal of epoxy resin by pyrolysis is an important issue in the view of metal recovery from printed circuit boards. Therefore, the results and methodology implemented in this work might be of interest in the field of electronic waste recycling.

CRediT authorship contribution statement

Zhiya Duan: Conceptualization, Methodology, Software, Validation, Investigation, Writing - original draft. **Olivier Fiquet:** Conceptualization, Methodology, Validation, Investigation, Resources. **Carine Ablitzer:** Conceptualization, Methodology, Validation, Supervision, Project administration, Funding acquisition. **Laurent Cassayre:** Conceptualization, Methodology, Writing - review & editing. **Hugues Vergnes:** Conceptualization, Methodology. **Pascal Floquet:** Conceptualization, Methodology, Software, Formal analysis, Writing - review & editing. **Xavier Joulia:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2020.123367>.

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