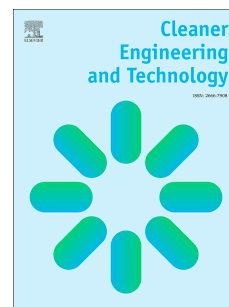


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Chemical recycling of plastics assisted by microwave multi-frequency heating

Alberto Frisa-Rubio^{1,*}, Carlos González-Niño¹, Patricia Royo^{1,4}, Nelson García-Polanco¹, David Martínez-Hernández¹, Lucía Royo-Pascual¹, Sven Fiesser², Ema Žagar³, Tatiana García-Armingol^{1,4}

¹Fundacion CIRCE—(Research Centre for Energy Resources and Consumption), Avenida Ranillas, Edificio Dinamiza 3D, 50018 Zaragoza, Spain

²Fricke und Mallah Microwave Technology GmbH, Peine, Germany

³Kemijski inštitut / National Institute of Chemistry, Ljubljana, Slovenia

⁴Instituto Universitario de Investigación Mixto CIRCE - (Fundacion CIRCE - Universidad de Zaragoza), Parque Empresarial Dinamiza, Avenida Ranillas 3D, 50018, Zaragoza, Spain

*corresponding author: afrisa@fcirce.es

ABSTRACT

Handling plastic waste through recycling allows extending the life of polymeric materials, avoiding recurrence to incineration or landfilling. In contrast with traditional mechanical recycling technologies, chemical recycling enables the obtention of the virgin monomers by means of depolymerisation to create new polymers with the same mechanical and thermal properties as the originals. Research presented in this paper is part of the *polynSPIRE* project (Horizon 2020 European funding programme) and develops and scales-up a heated reactor to carry out the depolymerisation of polyamide-6 (PA6), polyamide-6,6 (PA66) and polyurethane (PU) using microwave (MW) technology as the heating source. The purpose is to design and optimise a MW reactor using up to eight ports emitting electromagnetic waves. Finite element method (FEM) simulation and optimisation are used to design the reactor, considering as parameters the data obtained from experimental dielectric testing and lab-scale characterisation of the processes and materials studied. Two different COMSOL Multiphysics modules are involved in this work: Radio Frequency (RF) and Chemical Reaction Engineering (RE), to simulate the reactor cavity using two frequency levels (915 MHz and 2.45 GHz) with a power level of 46 kW, and the chemical depolymerisation process, respectively. A sensitivity study has been performed on key parameters such as the frequency, the number of ports, and position inside the reactor to consolidate the final design. It is expected that these results assist in the design and scale-up of microwave technology for the chemical recycling of plastics, and for the large-scale deployment of this sustainable recovery alternative.

KEYWORDS

Chemical recycling, plastic recycling, depolymerisation, microwave technology, FEM simulation, polyamide, polyurethane.

1. Introduction

Plastic-based materials are used in a wide range of applications due to their intrinsic properties such as weight reduction, chemical resistance and inertness, or price. Consequently, the global plastic demand is continuously increasing, amounting to 359 Mt in 2019. Likewise, plastic waste generation has increased correspondingly over the years, constituting a significant amount of material that could be used as a potential resource. However, despite efforts to adopt

a circular economy and to diversify recycling strategies, the recovery rate in Europe is still below 30%, being almost negligible in several sectors (PlasticsEurope, 2019).

Various reasons are behind the low rate of recycling in sectors different from the packaging sector. Particularly, progress in the engineering, automotive or electronic industry has brought about new material requirements which result in a heterogeneous composition. The presence of mixed streams hinders the efficiency of the conventional recycling infrastructure. In addition, small amounts of specific elements or components can interfere with proper recycling or reduce the economic value of the recycled material, making the process less cost-efficient (Hopewell et al., 2009).

Apart from the inherent technical limitations of existing technologies, achieving life cycle circularity using conventional mechanical recycling is not possible for certain sectors since the quality features of recycled polymers do not comply with the same standards as their virgin counterparts (Hopewell et al., 2009). This effect leads to the "downcycling" effect: recycled materials are used for low added value applications, reducing the solutions' economic profitability and hindering their proper deployment and market roll-out. To overcome this limitation, chemical recycling is presented as a promising route to recycle plastic material by transforming waste into monomers, allowing recovering the material's original properties. However, the current state of art of the method requires additional researching in terms of scalability and energy use (Rahimi and García, 2017).

Particularly, different routes of chemical recycling can be found in the literature for polyamides (PA) and polyurethanes (PU). For instance, PA can be depolymerised by hydrolysis, aminolysis (Polk, 2003), or alcoholysis ("A kind of alcoholysis recovery method of nylon 66 material," n.d.) (glycolysis (Kim et al., 2006) and methanolysis (Datta et al., 2018)). The method selection criteria depends on the polymeric structure. Several chemical methods of depolymerisation exist for PU and they are divided into hydrolysis, glycolysis, phosphorolysis, alcoholysis, aminolysis, and acidolysis. Among all these methods, microwave-assisted glycolysis and hydroglycolysis have been reported as the most promising pathways to shorten the reaction time compared to conventional heating (Polk, 2003). In this light, microwave (MW) irradiation is a well-established technique in organic synthesis (Lidström et al., 2001), including polymer synthesis (Achilias, 2014) and depolymerisation (Erdmenger, 2009). In contrast to other heating techniques, a major advantage of using MW is contactless instantaneous and rapid heating, resulting in faster reaction rates.

Consequently, the current work aims to present a new development of a chemical recycling application assisted by microwave heating to increase recyclability rates and circular economy. The present article provides tools to overcome the limitations associated with the large-scale implementation of this technology. An iterative design process has been performed evaluating the material heating inside a reactor using eight ports emitting electromagnetic waves. Although several works are available in the literature concerning single-frequency (S-F) simulation for different geometries and applications based on FEM simulation (Ethridge and Kaukler, 2014), design optimization of the applicators (Rajpurohit and Chhibber, 2016), numerical analysis of the resonant cavity (Nigar et al., 2019) or electric field optimisation (Santos et al., 2010).

there is scarcity research available concerning multi-frequency (M-F) simulation. Therefore, this paper focuses on the 3D simulation of a reactor cavity using two frequency levels (915 MHz and 2.45 GHz) with a maximum power level of 51 kW for PA and PU depolymerisation purposes. Although chemical recycling is already applied with success using MW to some polymers like PET (Raheem et al., 2019)(Ikenaga et al., 2016), poly(bisphenol-A carbonate) (Tsintzou et al., 2012) or polyester resins (Wang et al., 2020), a low number of papers are available regarding PA and PU. Finally, reaction kinetics were also simulated to recreate lab-scale experiments to verify that numeric modelling could accurately represent the mechanism. As a consequence of implementing chemical recycling with MW, the environmental impact can

be reduced thanks to a more efficient and sustainable chemical process and processing technologies. Plastic waste is used as “raw material” for the production of added value products, such as recyclable plastic materials or composites and chemicals but excluding fuels. Overall, the technologies developed in the polynSPIRE project are expected to provide a decreased utilisation of primary fossil resources in the process industry of at least 30% and a reduction of the associated CO₂ emissions of at least 20%.

2. Methodology

Overall, the present work studies PA and PU depolymerisation processes based on chemical reactions. The first step is to describe and identify chemical reactions to be carried out, adding chemical agents to degrade the polymer. The second step is to combine the heating to the mixing process, to speed up the chemical reaction. This work shows the introduction of microwave heating technology by MW reactor configuration. Using MWs as heating source promotes faster heating while conveying a more sustainable industrial process than conventional methodologies, reliant on fossil fuels.

2.1. Chemical reaction simulation

The optimal pathway for depolymerising the polymers under study was determined as part of the *polynSPIRE* project and is reported in the following reference (Češarek et al., 2020). Polyamide 6 (PA6) is depolymerised via hydrolysis into its reaction product, 6 aminocaproic acid hydrochloride. After chloride removal, the monomer 6 aminocaproic acid (6-ACA) is obtained. Polyamide 66 (PA66) is similarly depolymerised into adipic acid (AA) and hexamethylenediamine hydrochloride which, once the chloride is removed, becomes the monomer hexamethylenediamine (HMDA). Figure 1 and Figure 2 represent the general scheme of depolymerisation process for PA6 and PA66, respectively.

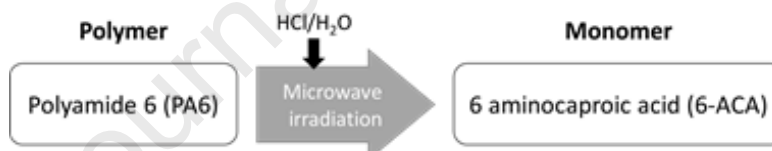


Figure 1. PA6 process scheme.

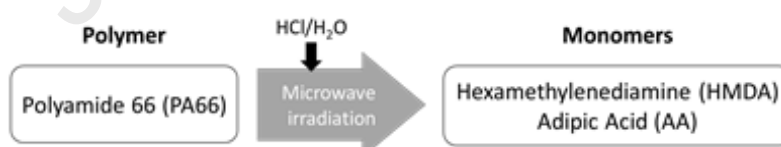


Figure 2. PA66 process scheme.

Polyurethane is depolymerised via hydroglycolysis, yielding polyol, diamine toluene (DAT) and carbon dioxide (CO₂) as reaction products. The global reaction of PU depolymerisation is shown in Figure 3.

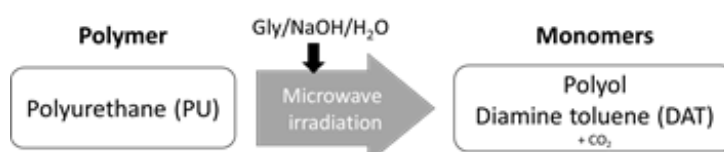


Figure 3. PU process scheme.

The reaction parameters for the hydrolysis of PA6 and PA66 catalysed by HCl, were determined through measuring the PA concentration with 1H NMR spectroscopy at different times and two

temperature levels: 170 and 190°C. An irreversible reaction mechanism with pseudo first order dependence on the polymer concentration has been assumed. The reaction kinetic constant (k) has been calculated therefore by plotting the natural logarithm of the polymer concentration against time and taking the slope of the curve. After evaluation at two distinct temperature levels, the reactions activation energies and Arrhenius constants were approximated through applying the well-known Arrhenius equation:

$$k = A e^{-\frac{E_a}{RT}} \quad (1)$$

where:

k : kinetic rate constant

A : Arrhenius factor

E_a : activation energy

R : ideal gas constant

T : absolute temperature

The methodology for the depolymerisation simulation of PA and PU is presented in Figure 4.



Figure 4. Methodology to develop reaction engineering simulation.

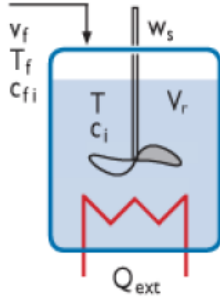
The methodology steps are described as follows:

1. **Chemical reaction definition:** In this step, the reactants and products of the reaction have been defined. Polymers, monomers, and the catalyst molar masses and densities were given input data in the COMSOL Multiphysics interface.
2. **Kinetics:** Results from the experimentation described before were used to characterise the reaction rates.
3. **COMSOL modelling:** The simulation has been parametrised contemplating parameters like volume of the solvent, initial concentration of species, temperatures, Arrhenius constant and filling procedure.
4. **Simulation & Results:** This section includes simulation results for the volumetric flow rate, reactor volume, concentration of species, polymer mass and monomer mass.

Table 1 shows the equations that have been used to simulate the reaction in COMSOL. As shown in this table, reaction rate, mass balance and volumetric production rate were used in the computation. As a first approximation, a perfectly mixed system has been considered. Accordingly, the reaction has been calibrated using a space-independent model.

Table 1. Reaction Engineering Equations.

Reaction rate	$r_1 = k_1 c_P$	(2)
Mass Balance	$\frac{d(c_i V_r)}{dt} = v_{f,i} c_{f,i} + R_i V_r$	(3)



**Volumetric
production rate
due to chemical
reaction**

$$\frac{dV_r}{dt} = \sum v_{f,i} + v_p$$

$$v_p = \sum_j \sum_i v_{ij} \frac{M_i}{p_i} r_{jv_r} \quad (4)$$

The parameters employed for the simulations can be observed in the respective columns of Table 2 for PA6, PA66 and PU simulations and Table 3 for properties of species used.

Table 2. Parameters for PA6, PA66 and PU simulation.

	<i>PA6 reaction</i>	<i>PA66 reaction</i>	<i>PU reaction</i>
Initial reactor volume	$8 \times 10^{-6} \text{ m}^3$	$8 \times 10^{-6} \text{ m}^3$	$7.97 \times 10^{-6} \text{ m}^3$
Inlet concentration			
PA6	$9,985.9 \text{ mol/m}^3$	-	-
PA66	-	$5,037.3 \text{ mol/m}^3$	-
PU	-	-	221.41 mol/m^3
<i>Final monomers</i>	0	0	0
HCl 5.56M	$5,560 \text{ mol/m}^3$	$5,560 \text{ mol/m}^3$	
DA 2%	-	-	626.7 mol/m^3
Water	-	-	$55,389 \text{ mol/m}^3$
Maximum volumetric feed rate	$1.765 \text{ m}^3/\text{s}$	$2.28 \times 10^{-7} \text{ m}^3/\text{s}$	$6.52 \times 10^{-8} \text{ m}^3/\text{s}$
Time for shift in feed	20.5 s	20 s	20 s
Frequency factor	2.92×10^{24}	1.79×10^{14}	1.79×10^{14}
Activation Energy	$1.9471 \times 10^5 \text{ J/mol}$	$1.0476 \times 10^5 \text{ J/mol}$	$1.0476 \times 10^5 \text{ J/mol}$
Kinetic constant value	0.0032 L/s		0.0063826 L/s
Temperature of the reaction	443.15 K	443.15 K	503.15 K
Ideal gas constant	$8.314 \text{ J/(mol} \cdot \text{K)}$		

Table 3. Properties of the different species used in the simulation.

<i>Substance</i>	<i>Molar mass (kg/mol)</i>	<i>Density (kg/m³)</i>
Water	0.018	997
HCl 5,56M	-	1,090
DA 2%	-	1,253.4
PA6	0.11316	1,130 (Mark, 2007)
PA66	0.22631	1,140
PU	5.194	1,150
6-ACA	0.16763 (PubChem, n.d.)	1,131.3 (ChemicalBook, n.d.)
HMDA	0.18913	890

AA	<i>0.14614</i>	<i>1,360</i>
Polyol	<i>3.5</i>	<i>1,020</i>
DAT	<i>0.12217</i>	<i>1,260</i>
CO₂	<i>0.044</i>	<i>1.98</i>

Parameters such as the initial reactor volume, the maximum volumetric feed rate, the control fill parameter, and the kinetic constant parameters are defined as inputs within the software interface.

2.2. Reaction Engineering (RE) simulation

Following the methodology presented in **Error! Reference source not found.**, the reaction of PA6, and PU were simulated using COMSOL. To obtain the necessary parameters for the simulations, kinetic constants were calculated assuming a pseudo-first order reaction and Arrhenius parameters approximated by linear regression from plots of $\ln k$ versus temperature. Figure 5 and Figure 6 shows there is a fair correspondence of the depolymerisation process to a pseudo first order reaction for all polymers considered. As expected, when operating at a higher temperature the kinetic constants are 10 and ~ 3.5 times higher for PA-6 and PA-66, respectively. Reaction times are also significantly reduced.

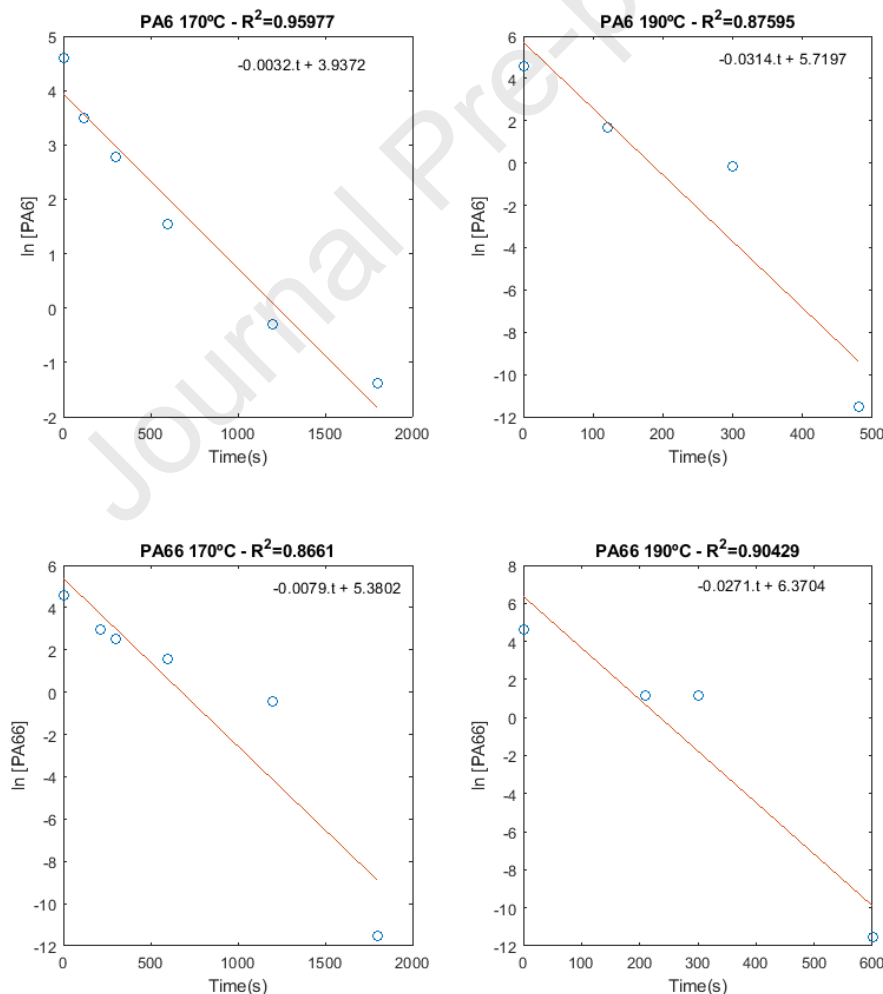


Figure 5. Depolymerisation kinetics of PA6 and PA66 at 170°C and 190°C.

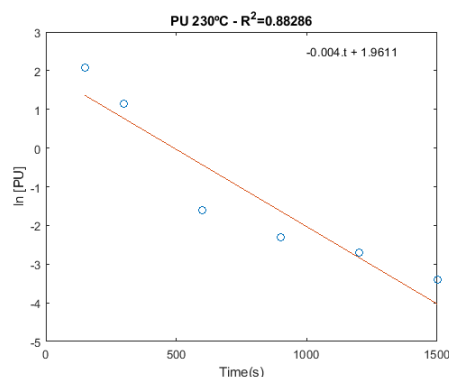


Figure 6. Depolymerisation kinetics of PU at 230°C.

From obtained correlations, Table 4 shows each pseudo-first order reaction constant:

Table 4. Summary of reaction constants obtained for all considered polymers.

Polymer	Temperature (°C)	Pseudo-first order reaction constant (1/s)
PA-6	170	0.0032
PA-6	190	0.0314
PA-66	170	0.0079
PA-66	190	0.027
PU	230	0.004

Recreating the same conditions as on a laboratory scale, the simulation has been performed using $0.1765 \text{ cm}^3/\text{s}$ volumetric flow rate. The polymer feed is shut off once the reactor volume reaches 11.53 cm^3 , which occurs after 20 s. The reaction is then allowed to go to completion. The volumetric feed has been computed in order to obtain the polymer volume during the time frame imposed in the computation. Both temperatures required similar volumetric rate.

The reactor volume is presented in Figure 7 as a function of reaction time. It can be seen the progress for the two temperatures, 170 °C and 190 °C. In both cases the curves evolves similarly up to $11.53 \times 10^{-6} \text{ m}^3$, which is the sum of volumes of the reactant and the catalyst and then, it starts the chemical reaction, therefore, the volume increases according to the relation between properties of the products and the reactants, defined in the parameters. As shown in Figure 7, the final state is the same for both temperatures, however the dynamics are different, faster for the higher temperature case, which is in accordance with the kinetics.

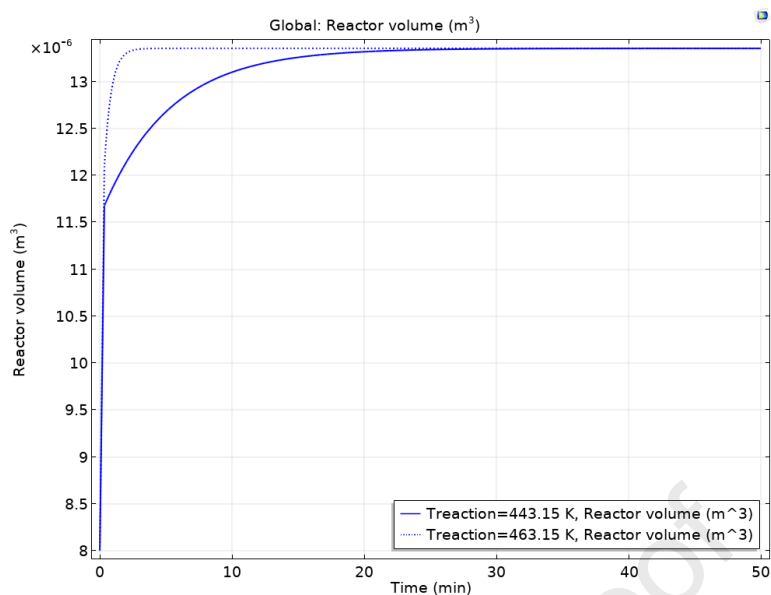


Figure 7. Reactor volume (m^3) in function of the time (min) for two different reaction temperatures.

Concentration of Species

Figure 8 shows the degree of PA6 degradation as a function of time at temperatures of 170 °C and 190 °C as determined by ^1H NMR. Figure 9 illustrates the results obtained from the simulation for the concentration of species (polymer, monomer, and catalyst) with two temperature levels 170 °C and 190 °C. Similar trends comparing experimental and simulation are found. The concentration of polymer reduces, while the concentration of monomer increases according to their definition in the parameters.

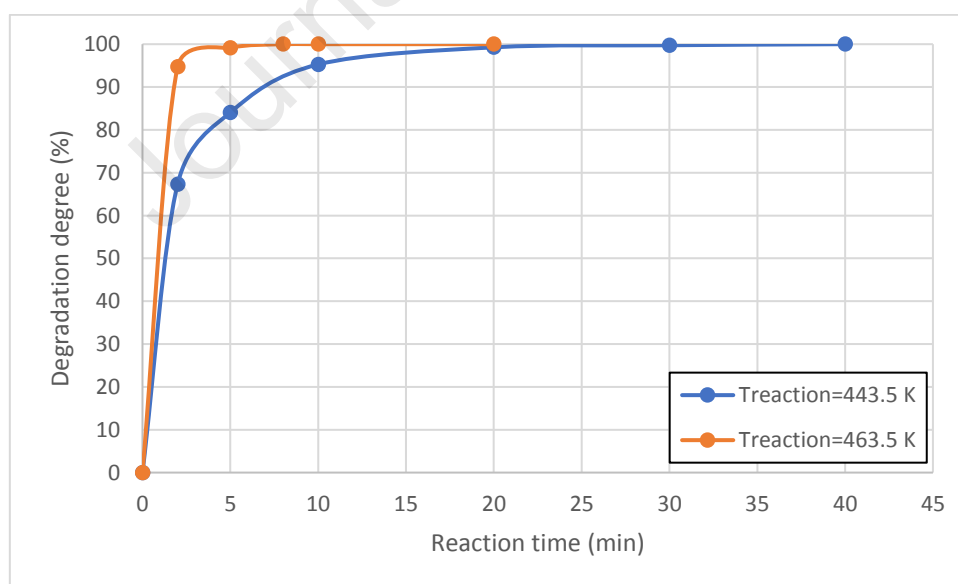


Figure 8. Experimental values for degree of PA6 degradation vs. time determined at 170 and 190°C reaction temperatures.

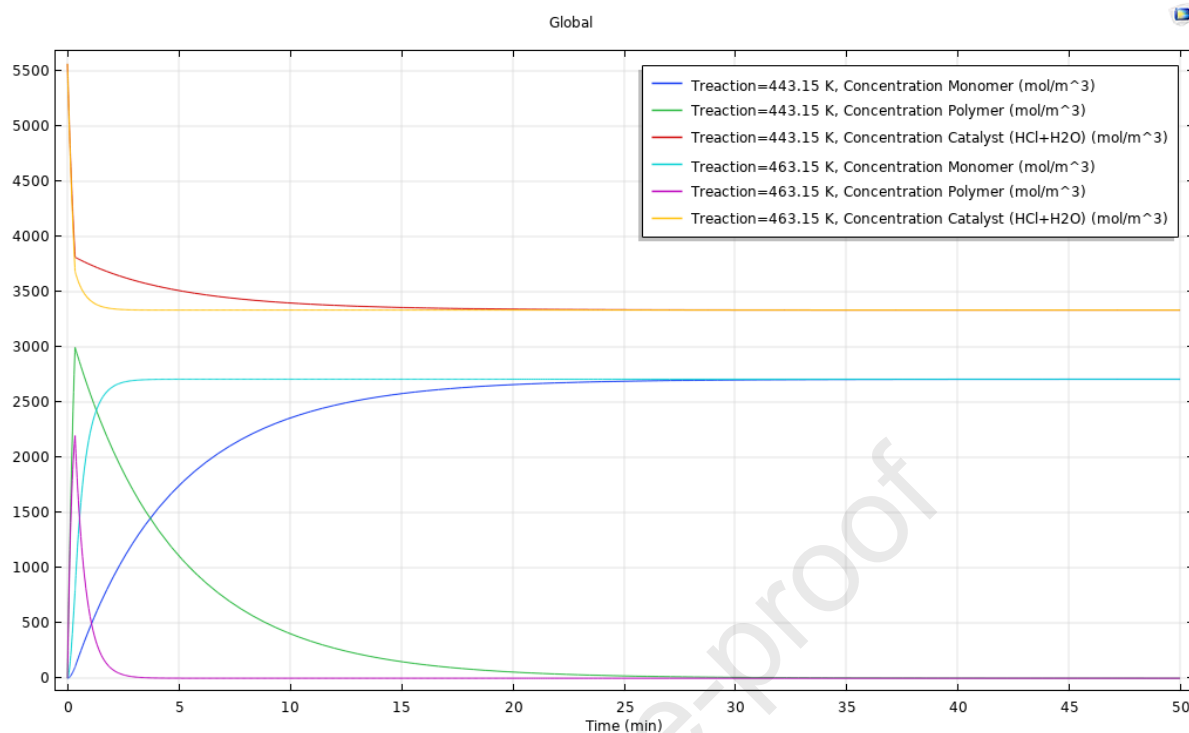


Figure 9. Concentration of species (mol/m^3) of PA6 in function of the time (min) for two different reaction temperatures.

Polymer Mass

In order to validate the computation, the polymer mass evolution has been extracted from COMSOL and illustrated in Figure 10 (blue coloured lines). These results are compared with experimental values for the two temperature levels of temperature. According to the experimental procedure, the initial mass of polymer is 4 g, obtaining results with an accuracy of up to 95% in terms of the reaction time.

Monomer Mass

To conclude the results, the mass of monomer has been extracted from COMSOL, and illustrated in Figure 10 (red coloured lines). It enables to summarise the relation between the inlet reactants and the products obtained after the reaction.

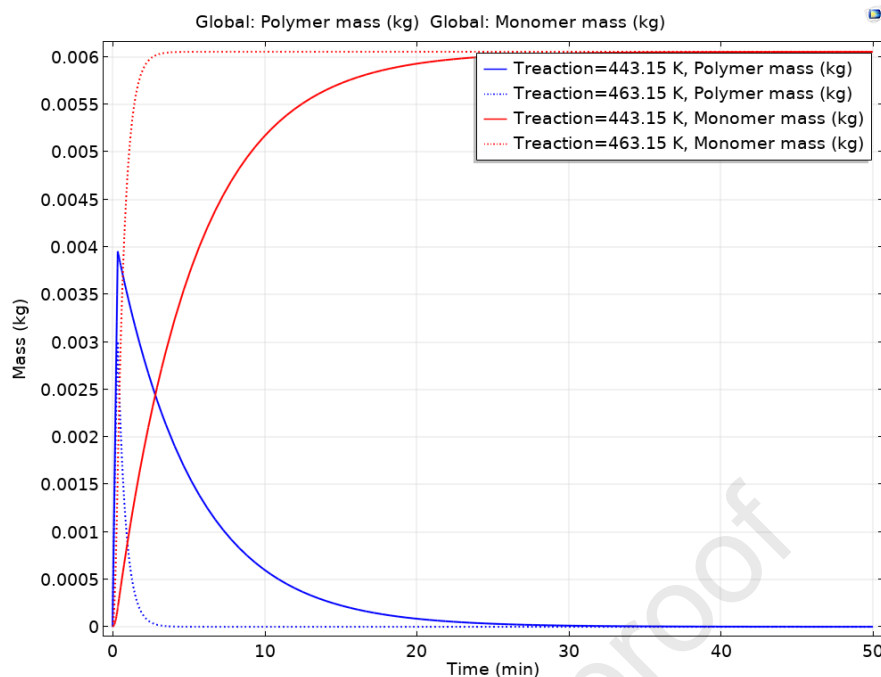


Figure 10. Polymer and monomer mass (kg) in function of the time (min) for two different reaction temperatures.

On the one hand, parameters such as the initial reactor volume, the maximum volumetric feed rate, the control fill parameter, and the kinetic constant parameters are defined as inputs within the software interface. And on the other hand, variables such as volumetric feed rate, monomer and polymer masses were monitored and analysed after the simulation. A parametric analysis combining different pressure and temperature levels have been tested based on the operation conditions reported in (Češarek et al., 2020), all yielding to the same degree of conversion, i.e., monomer recovery. Table 5 summarises the different evaluated scenarios.

Table 5. Experimental conditions for COMSOL Multiphysics simulation.

Depolymerisation product	Operating temperature (°C)	Operating pressure (bar)	Operating time (min)
PA6	170	4.6	40
PA6	190	10	8
PA66	170	4.6	30
PA66	190	10	10
PU	230	5.8	40

2.3. Microwave design and simulation

Several simplified configurations were analysed to select the most adequate in terms of manufacturing feasibility, operation mode and energy distribution. The criteria adopted for making a decision on the most suitable choice to carry out the reactions of interest were:

- ✓ Ability to handle high-pressure loads
- ✓ Homogeneous energy distribution
- ✓ Complexity of manufacturing

The most restrictive operating conditions for the reactor are expected during PA depolymerisation, as they require a pressure higher than 10 bar and a working temperature range of 200°C. Furthermore, the reactor material must withstand an acid atmosphere as HCl is needed for the depolymerisation reactions. The reactant and solvent for PA hydrolysis is H₂O, while

HCl serves as a catalyst that also reacts with the amine group of ACA and HMDA to form a salt. During PU depolymerisation by hydroglycolysis, a higher operation temperature (230°C) is required.

Multifrequency application

Due to restrictions and specifications of the chemical process carried out, it was decided to implement a resonant cavity as a chemical reactor, capable of operating at the two most widespread microwave frequencies, both 2.45 GHz and 915 MHz.

The potential advantage of using a multi-frequency reactor is directly related to the reactor's volumetric character. By heating the reactor's content with a single-frequency microwave generator the temperature of the content increases as a whole, but the temperature distribution will be uneven due to the geometrical properties and the penetration depth of the applied microwaves. Detailed investigations of the behaviour of the microwave radiation upon coupling in solid bodies have had the result that the penetration depth of the microwave radiation inversely proportionally decreases with increasing frequencies. Thus, the higher the frequency of the microwave radiation used, the lower the penetration depth. In this context it has also been found that the heat generation within the objects to be heated is more strongly concentrated within the surface ranges with higher frequencies of the microwave radiation used, when the dielectric properties of the objects to be heated are kept constant (Mallah, 2009). The use of several microwave generators with different frequencies and penetration depths is proposed in order to homogenise the temperature distribution.

2.4. Governing equations

The Maxwell's equations, the Poynting theorem and the energy conservation law are included in the Radio Frequency (RF) module and used to simulate the electromagnetic heating process. Assuming a time-harmonic EM field, Maxwell's equations are formulated as shown in Eq.(5):

$$\nabla \times \left(\frac{1}{\mu} \nabla \times \vec{E} \right) - (\omega^2 \varepsilon - i\omega\sigma) \vec{E} = \vec{0} \quad (5)$$

where ω is the angular velocity, σ is the electrical conductivity and \vec{E} is the complex-valued electric field. The electromagnetic losses considered in the model were the addition of the resistive and magnetic losses, presented in Eq.(6) and Eq.(7) respectively:

$$Q_{rh} = \frac{1}{2} \text{Re}(\vec{J} \vec{E}^*) \quad (6)$$

$$Q_{ml} = \frac{1}{2} \text{Re}(i\omega \vec{B} \vec{H}^*) \quad (7)$$

Where \vec{J} is the current density, \vec{B} is the magnetic flux density, and \vec{H} is the magnetic field intensity.

Heat transfer in a fluid

Two heat transfer mechanisms are considered in our model - convection and diffusion. Due to the fluid motion, three contributions to the heat equation are included:

- The transport of fluid implies energy transport, which appears in the heat equation as the convective contribution. Depending on the thermal properties on the fluid and on the flow regime, either the convective or the conductive heat transfer can dominate.
- The viscous effects of the fluid flow produce fluid heating. This term is often neglected; nevertheless, its contribution is noticeable for fast flow in viscous fluids.
- As soon as a fluid density is temperature-dependent, a pressure work term contributes to the heat equation.

Accounting for these contributions, in addition to conduction, results in the following Eq.(8), representing the transient heat equation for the temperature field in a fluid:

$$c_p \rho \frac{dT}{dt} + \rho c_p u \cdot \nabla T = \alpha_p T \left(\frac{\partial p}{\partial t} + u \cdot \nabla p \right) + \tau : S + \nabla \cdot (k \nabla T) + q \quad (8)$$

The equations above, Eq.(5-8), are introduced in the multiphysics model to solve the microwave-assisted heating process. Then, a description of the multiphysics coupling used in the different models, is shown below:

- Electromagnetic waves (frequency domain): the solver first step was to calculate the frequency domain (for the indicated domains), thus obtaining the electrical values that allow to convert the transmitted power into heat, by applying the Poynting vector.
- Heat transfer in fluids (time dependent): the mixture is modelled as a fluid because its behaviour will be closer to a liquid. For each time studied, the model will apply heat transfer conditions over the material domain.
- Electromagnetic, time-dependent heating: it is the coupling of both indicated physics, for each time studied, the solver evaluates the energy transferred to each mesh element according to the heat transfer limit conditions.

2.5. Assumptions and constraints

The assumptions considered are:

- Feeding system able to introduce the raw material in the process. The conceptual design indicates two different inputs for polymer material and liquid material. For simulation modelling, the vessel is considered is filled being operated by batch.
- Vessel/applicator where chemical reactions occur is assumed to achieve a semi-industrial operation volume, but extra parameters such as commercial materials and budget are accounted for.
- Cylindrical cavity, also called resonant cavity, with a volume of 1 m³. Additionally, different reactor shapes were studied in order to come up with an optimal design.
- Microwave generation equipment frequency and power of the generators). The reactor system integrates the following number of power emisors:
 - a. Three microwave generators of 2.45 GHz frequency and 6 kW power each one. Additionally, each microwave generator integrates a splitter system to introduce the emitted power into the cavity.
 - b. One microwave generator of 915 MHz frequency and 5 kW of power. Additionally, the microwave generator integrates a splitter system to introduce the emitted power into the cavity.

The constraints represent limitations and conditionate to the work development:

- The global operation volume of the system should ensure at least 300 L, by using three connected reactors of 100 L each one, as a feasible solution from the point of view of the availability of materials. Therefore, the modelling can be reduced to study just one reactor behaviour.
- Mixing substances such as HCl (Hydrochloric acid) requires avoiding commercial materials liable to be corroded for their use in the vessel.
- Operation pressure: depolymerisation laboratory tests have shown that the highest pressure level during operation is 10 bar for PA6 and PA66 (pressure is lower for PU). This implies the need for a robust system to ensure safe operating conditions.

3. Results

3.1. Conceptual design of the MW reactor and resonant cavity.

A cylindrical shape both reactor and vessel have been defined, connecting transmitting MW energy from ports to cavity connected through waveguides. A diagram of this configuration is presented in Figure 11.

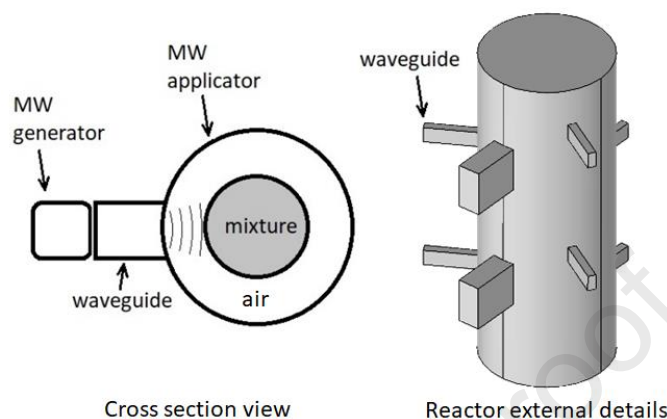


Figure 11. Conceptual design of the MW reactor.

The main physical characteristics of the conceptual design for the MW reactor are:

- ✓ Cylindrical cavity
- ✓ Cylindrical interior vessel
- ✓ 60° and 120° distribution of applicator ports
- ✓ Semi-batch operation
- ✓ Direct load of material

Before the final configuration shown, others were evaluated focused on following parameters: reactor shape and format, dimensions and distribution of the MW applicator ports, but always maintaining the same global microwave emission power which will affect to the processing of the chemical depolymerization.

About reactor shape and format, an hexagonal structure was modelled and tested but their advantages were not sufficient in contrast to its greater manufacturing complexity. In the same line, a cylindrical structure tested with tapered ends does not provide significant improvements in the distribution of energy within the reactor. For this reason a normal cylindrical reactor was selected optimizing the diameter.

Reactor height dimensions was restringed basically due to commercial vessel sizes, but it is important to define the position and power of each MW applicator port. Considering MF operation by using 3 power generators of 2.45 GHz and 6 kW each one, and one power generator of 915 MHz and 5 KW, it is decide for each generator to include an splitter system introducing, for each generator, the same power in two different points, obtaining a first improvement in homogeneous distribution of the energy inside the cavity. Considering this framework, the following results have been obtained from the Multiphysics simulation.

3.2. Radio Frequency (RF) simulation: electric results.

Different simulations were carried out to compare the performance of the different frequency ports on their own, and of their combined effect.

Figure 12 presents different cross sections of the vessel, showing the electric field norm that is directly related to the electromagnetic losses that induce the heating. Three different cases were evaluated, maintaining a total power of 23 kW in every case.

- 1- Simulations at 915 MHz: Large elongated zones of high intensity electric field are generated at the heights of the ports. These modes result in a high mean electric field of 4,936 V/m in the vessel. The standard deviation of the distribution amounts to 2,027 V/m. Standard deviation is used in this context as a measure of the homogeneity of the field, with lower standard deviations indicating more homogeneous fields.
- 2- Simulations at 2.45 GHz: A more homogeneous application of the electric field is achieved by solely using the six 2.45 GHz ports. It can be observed that the high intensity regions are scattered in small zones along the vessel. The mean is lower to that of the previous case 2765.2 V/m, and so is the standard deviation 986 V/m.
- 3- When combining both frequencies, the reactor achieves a more homogeneous distribution in the vessel, both in inner and outer areas. In addition, the electric field values increased when compared to those obtained in the previous case. The values of the mean and standard distribution are of 3,355 V/m and of 891.8 V/m in this case, respectively.

Graphical representations of the resulting electric fields are shown in

Figure 12. Considering the numerical results, the system working at 915 MHz is able to produce the strongest field with a mean of almost 5,000 V/m in the vessel, at the cost of a very low uniformity. When using solely the 2.45 GHz ports, the field becomes more homogeneous, but the strength of the field is reduced by 44%. Finally, when both frequencies are combined, the resulting field is the most uniform out of those considered, with the cost in terms of intensity (32%) being less than when solely using 2.45 GHz.

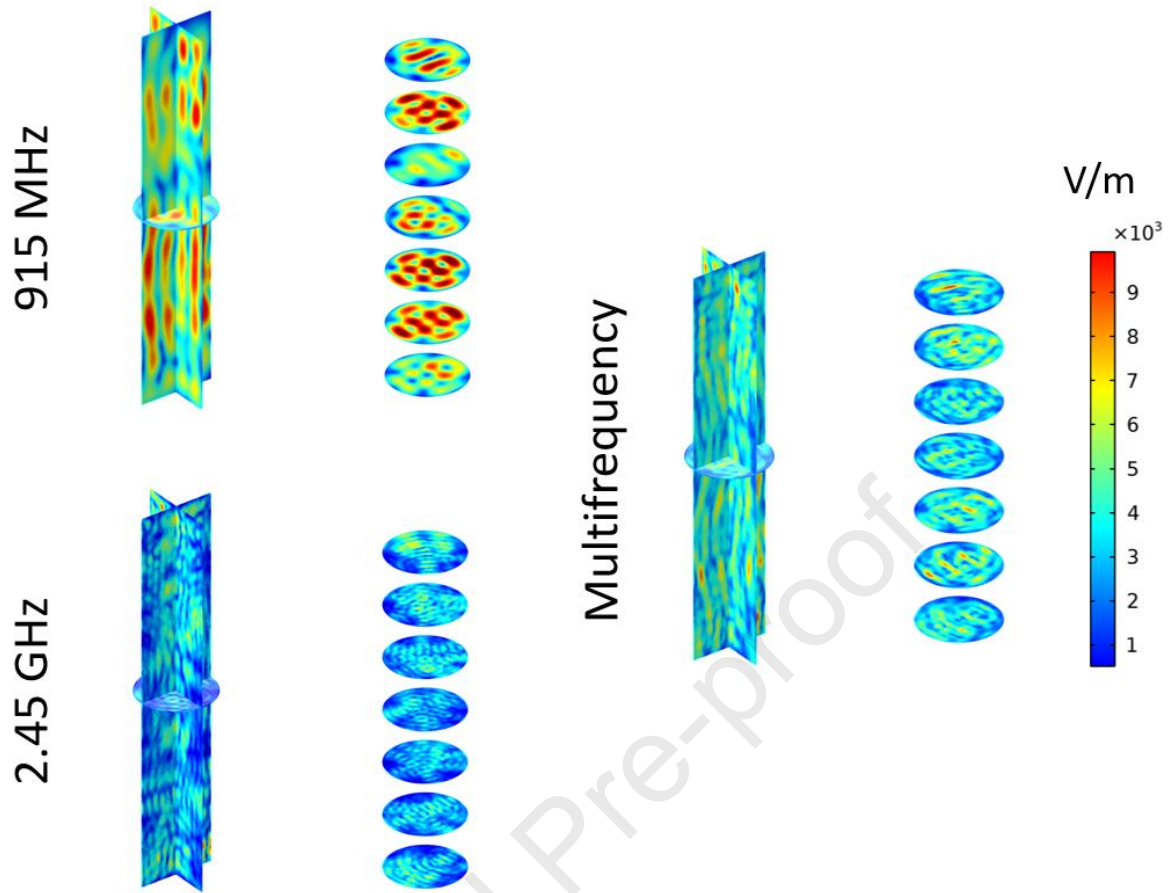


Figure 12. Electric field norm (V/m) comparative by using single or coupled frequencies. Longitudinal sections and Z-axis cross-section.

Attending to the generation of hot and cold points, different results can be observed in the cross-section represented in Figure 13, considering the same power level.

- (a) 915 MHz simulations: Specific hot points are found; whereas the central part is not absorbing energy from the MW source.
- (b) 2.45 GHz simulations: Penetration depth of the wave is lower than the obtained for the 915 MHz simulations, but hot points are avoided.
- (c) By combining frequencies, each of the ten slices along the vessel are much more similar than in previous case studies.

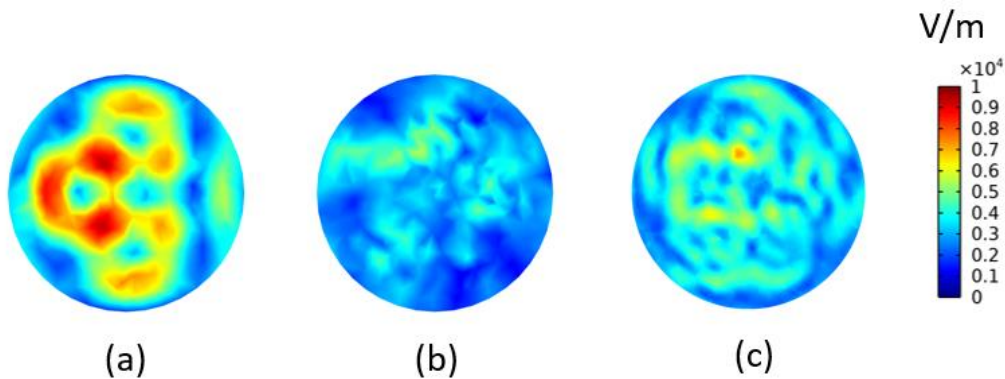


Figure 13. Electric field norm (V/m) comparative by using single frequency (a) 915 MHz and (b) 2.45 GHz or (c) coupled frequencies. Z-axis cross-section at 0.9 m from the reactor floor.

3.3. Radio Frequency (RF) simulation: thermal results.

Once the analysis of the electromagnetic waves was completed, a time-dependent heat transfer study followed, contemplating two different scenarios. For the first one, a static material was considered, where the spatial distribution of the electromagnetic losses led to a highly uneven temperature distribution with scattered hotspots that does not ensure uniformity of processing conditions in the batch (Figure 14, left). These temperature maps closely resemble the electromagnetic heat loss that is the heat source of the MW system. For the second scenario, the dielectric properties were kept the same as in the first scenario but the content of the reservoir was modeled as fluid in motion, leading to an almost homogeneous temperature field in the vessel (Figure 14, right), highlighting the dramatic effect that the inclusion of a mixer has in the temperature distribution.

The feasibility of reaching the temperature targets set in the chemical simulation stage in a feasible time frame, along with the homogeneity of temperature achieved in the vessel -both by means of the multifrequency heating and of the inclusion of a stirrer-, gives confidence that the system is appropriate for the recycling of all polymers taken into account (Table 5).

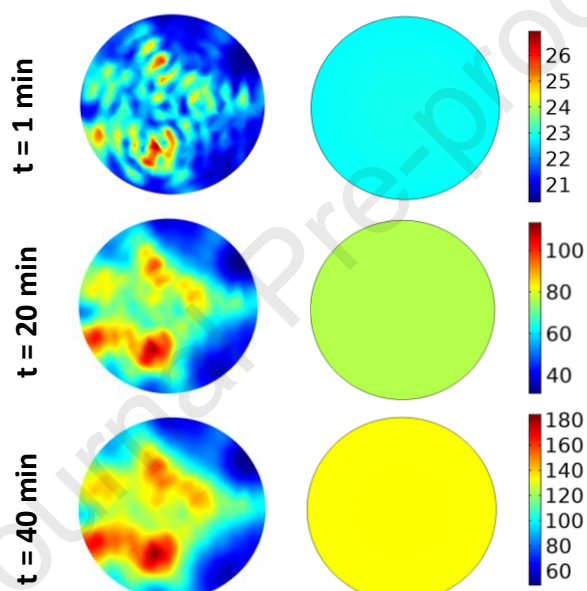


Figure 14. Comparison between the different temperature (°C) distributions in a cross-section (1 m from the bottom of the reactor) at time intervals = 1, 20 and 40 min for a model considering a static material subject to heating (left column) and a fluid moving in the reservoir (right column).

4. Conclusion

A complex physical system was reduced to two different mathematical models, taking advantage in the design stage and process configuration. The result establishes the basis for developing a new microwave system focused on a novel industrial process for polymer chemical recycling purposes based on microwave system as heating source.

A complete simulation methodology for depolymerisation of PA6 by means of experimental kinetics measurements analysis and simulation results of the reaction were presented. As a first approximation, a perfectly mixed system were considered and the reaction was calibrated using a space-independent model. Two temperature levels (170 °C and 190 °C) were used in order to obtain the simulation results in accordance with experimental measurements. Validation of simulation results for the time required to complete the reaction and the starting mass of polymer to be depolymerised showed great agreement with the experimental data, with differences lower than 5%.

Then, previous chemical development allowed to establish the main operating conditions on which to optimize a scaled design of a 100-liter chemical reactor operated by microwave. RF simulations results allowed analysing the thermal behaviour of the sample under different MW configurations obtaining selected temperatures of 170 °C and 190 °C in the expected times (less than 40 minutes). A comprehensive sensitivity study analysis was conducted varying the frequency, the number of applicator ports of the MW energy and the position. In this sense, the results presented revealed that combining MW frequencies (915 MHz and 2.45 GHz) is the most promising strategy to improve the homogenisation of the electromagnetic field distribution, whose mean value is 3,355 V/m for this case. It achieved a more homogeneous temperature than applying one frequency level, minimising the hotspots presence that hinder the reaction. The integration of a moving element (mixers) inside the cavity resulted in a very uniform temperature distribution, meaning a gradual and homogeneous heating process. In addition, the presented MW technology allows a significant reduction of heating time between 40% - 80% compared to convection heating technologies, because direct heating occurs over chemical compounds that are highly susceptible to heating by microwave radiation; thus, leading to an increase in the process's overall efficiency.

Future efforts will address the total coupling between heating and chemical process with the aim of simulating the interaction of the MW heating with the chemical reactions. This will provide more realistic results and a better understanding of the process. Moreover, other aspect to be further performed are the life cycle assessment (LCA), the life cycle costs (LCC) and the techno-economic (TE) analysis to demonstrate that POLYNSPIRE can bring environmental benefits compared to current SoA technologies and solutions for plastic recycling.

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NOMENCLATURE

6-ACA – 6 aminocaproic acid

¹H NMR – Proton nuclear magnetic resonance

HCl – Hydrochloric acid

HMDA – Hexamethylenediamine

M-F – Multi-frequency

MW – Microwave

PA – Polyamide

PU – Polyurethane

S-F – Single-frequency simulation

c_i – Species molar concentration (SI unit: mol/m³)

$c_{f,i}$ – Species concentration (SI unit: mol/m³) of the associated feed stream

$v_{f,i}$ – Feed Stream volume flow rate (SI unit: m³/s)

R_i – Reaction rate of species i (SI unit: mol/(m³·s))

V_r – Reactor volume (SI unit: m³)

v_p – Volumetric production rate due to chemical reaction (SI unit: m³/s)

v_{ij} – Stoichiometric coefficient of species i in reaction j

M_i – Species Molecular Weight (SI unit: kg/mol)

ρ_i – Species density (SI unit: kg/m³)
 r_j – Reaction rate (SI unit: mol/(m³·s))
 μ – Magnetic permeability (SI unit: H/m)
 E – Electric field (SI unit: V/m)
 ω – Angular frequency (SI unit: rad/s)
 ε – Permittivity (SI unit: F/m)
 i – Unit imaginary number
 J – Current density (SI unit: A/m²)
 B – Magnetic flux density (SI unit: T)
 H – Magnetic field (SI unit: A/m)
 c_p – Specific heat capacity at constant pressure (SI unit: J/(kg·K))
 T – Temperature (SI unit: K)
 u – Velocity vector (SI unit: m/s)
 α_p – Coefficient of thermal expansion (SI unit: 1/K)
 p – Pressure (SI unit: Pa)
 τ – Viscous stress tensor (SI unit: Pa)
 k – Thermal conductivity (SI unit: W/(m·K))
 q – Heat sources other than viscous dissipation (SI unit: W/m³)

References

- A kind of alcoholysis recovery method of nylon 66 material, n.d. . CN107056624B.
- Achilias, D., 2014. Polymer Degradation Under Microwave Irradiation.
- Češarek, U., Pahovnik, D., Žagar, E., 2020. Chemical Recycling of Aliphatic Polyamides by Microwave-Assisted Hydrolysis for Efficient Monomer Recovery. *ACS Sustain. Chem. Eng.* 8, 16274–16282. <https://doi.org/10.1021/acssuschemeng.0c05706>
- Chemical Book CAS Database: 6-Aminocaproic acid [WWW Document]. URL https://www.chemicalbook.com/ChemicalProductProperty_EN_CB5223888.htm
- Datta, J., Błażek, K., Włoch, M., Bukowski, R., 2018. A New Approach to Chemical Recycling of Polyamide 6.6 and Synthesis of Polyurethanes with Recovered Intermediates. *J. Polym. Environ.* 26, 4415–4429. <https://doi.org/10.1007/s10924-018-1314-4>
- Erdmenger, T., 2009. Alternative routes and solvents in polymer chemistry: microwave irradiation and ionic liquids. Eindhoven University of Technology. <https://doi.org/https://doi.org/10.6100/IR643858>
- Ethridge, E., Kaukler, W., 2014. Finite Element Analysis of Three Methods for Microwave Heating of Planetary Surfaces. <https://doi.org/10.2514/6.2012-801>
- Hopewell, J., Dvorak, R., Kosior, E., 2009. Plastics recycling: Challenges and opportunities. *Philos. Trans. R. Soc. B Biol. Sci.* 364, 2115–2126. <https://doi.org/10.1098/rstb.2008.0311>
- Ikenaga, K., Inoue, T., Kusakabe, K., 2016. Hydrolysis of PET by Combining Direct Microwave Heating with High Pressure. *Procedia Eng.* 148, 314–318. <https://doi.org/https://doi.org/10.1016/j.proeng.2016.06.442>
- Kim, K.J., Dhevi, D.M., Lee, J.S., Cho, Y.D., Choe, E.K., 2006. Mechanism of glycolysis of nylon 6,6 and its model compound by ethylene glycol. *Polym. Degrad. Stab.* 91, 1545–1555. <https://doi.org/https://doi.org/10.1016/j.polymdegradstab.2005.09.019>
- Lidström, P., Tierney, J., Wathey, B., Westman, J., 2001. Microwave assisted organic synthesis—a review. *Tetrahedron* 57, 9225–9283. [https://doi.org/https://doi.org/10.1016/S0040-4020\(01\)00906-1](https://doi.org/https://doi.org/10.1016/S0040-4020(01)00906-1)
- Mallah, M., 2009. Microwave Heater. US20090302031A1.

- Mark, J.E., 2007. Physical properties of polymers handbook. Springer, New York.
- Nigar, H., Sturm, G.S.J., Garcia-Baños, B., Peñaranda-Foix, F.L., Catalá-Civera, J.M., Mallada, R., Stankiewicz, A., Santamaría, J., 2019. Numerical analysis of microwave heating cavity: Combining electromagnetic energy, heat transfer and fluid dynamics for a NaY zeolite fixed-bed. *Appl. Therm. Eng.* 155, 226–238. <https://doi.org/10.1016/j.applthermaleng.2019.03.117>
- PlasticsEurope, 2019. Plastics - the Facts 2019. An analysis of European plastics production, demand and waste data.
- Polk, M.B., 2003. Depolymerization and Recycling. *Synth. Methods Step- Growth Polym.*, Wiley Online Books. <https://doi.org/10.1002/0471220523.ch10>
- PubChem Compound Summary for CID 564, Aminocaproic acid [WWW Document]. Natl. Cent. Biotechnol. Inf. URL <https://pubchem.ncbi.nlm.nih.gov/compound/Aminocaproic-acid>
- Raheem, A.B., Noor, Z.Z., Hassan, A., Abd Hamid, M.K., Samsudin, S.A., Sabeen, A.H., 2019. Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: A review. *J. Clean. Prod.* 225, 1052–1064. <https://doi.org/10.1016/j.jclepro.2019.04.019>
- Rahimi, A., García, J.M., 2017. Chemical recycling of waste plastics for new materials production. *Nat. Rev. Chem.* 1, 46. <https://doi.org/10.1038/s41570-017-0046>
- Rajpurohit, D.S., Chhibber, R., 2016. Design Optimization of Two Input Multimode Applicator for Efficient Microwave Heating. *Int. J. Adv. Microw. Technol.* 1, 68–73.
- Santos, T., Costa, L., Valente, M., 2010. 3D electromagnetic field simulation in microwave ovens: a tool to control thermal runaway. *COMSOL Conf.* 3–7.
- Tsintzou, G.P., Antonakou, E. V, Achilias, D.S., 2012. Environmentally friendly chemical recycling of poly(bisphenol-A carbonate) through phase transfer-catalysed alkaline hydrolysis under microwave irradiation. *J. Hazard. Mater.* 241–242, 137–145. <https://doi.org/10.1016/j.jhazmat.2012.09.027>
- Wang, X.-L., An, W.-L., Tian, F., Yang, Y., Xu, H.-X., Wang, D., Zhao, X., Xu, P.-P., Xu, S., Wang, Y.-Z., 2020. Fast microwave-assisted hydrolysis of unsaturated polyester resin into column packing for rapid purifying of dye wastewater. *J. Hazard. Mater.* 384, 121465. <https://doi.org/10.1016/j.jhazmat.2019.121465>

HIGHLIGHTS

- An efficient and intensive microwave technology is used for chemical recycling.
- The reactor performance is analysed for PA and PU depolymerisation purposes.
- Numerical simulation assists the electromagnetic design and microwave configuration.
- Multi-frequency 3D simulation assess the frequency level and power (up to 51 kW).
- Chemical reactions for chemical recycling are tested in laboratory for validation.

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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