17th International Conference on Microwave and High Frequency Heating
Valencia, Spain, September 9-12, 2019
AMPERE 2019
ISBN: 978-84-9048-719-8
DOI: http://dx.doi.org/10.4995/Ampere2019.2019.9901

DEVELOPING MICROWAVE CHEMISTRY UNDER PROCESS ENGINEERING PRINCIPLES

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Keywords: microwave, radio-frequency heating, power applications

Introduction

It is nowadays admitted that microwaves are frequently used in organic chemistry labs [1] (even if not as much as it was predicted 20 years ago, one must say [2]). On the other side it is also certain that this technology has not yet found its place in chemical industry: application at a production scale are very scarce [3][4] and this despite the potential advantages of the technology (selective heating, high heating rate, low thermal inertia…). We believe the main reason for this is that mastering all the aspects of microwaves assisted synthesis at industrial scale demands a lot of different skills to work together: chemistry, process engineering, microwave engineering, materials science. This is so challenging that tools and methodologies for quantification of industrial microwave interest and scaling-up of lab results are missing.
The activity of Processium consists in selecting and sizing for its clients the most suitable reaction and separation techniques (and technologies) for a given process (i.e. to go from feed composition A to on-spec product composition B). It is therefore essential for this type of business to be able to analyze and compare a wide range of technologies, including innovative ones like microwave synthesis.
An overview on how microwave synthesis technology is integrated by Processium into the range of technologies available to its customers is given in this article.

Each technology has its use: In which case microwaves are useful? When are they useless?

No matter the unit operation (reaction, distillation, liquid-liquid extraction…) every technology has its own limits of application depending mainly on:

- Operating conditions
- Physico-chemical properties of the feed
- Kinetics of the reaction
- Thermodynamics of phase equilibria

Outside these limits, other technologies are more advantageous or even more easily applicable.
Rationalization of the range of applicability of each technology is key for selecting the best one. This kind of work has not been found in literature for microwave assisted organic chemistry. An example of a methodology to guide into the selection of microwave assisted synthesis is given in Fig. 1.
It should be noted that all the results presented here are based on the widely accepted assumption that microwaves simply consist of a means of heating.

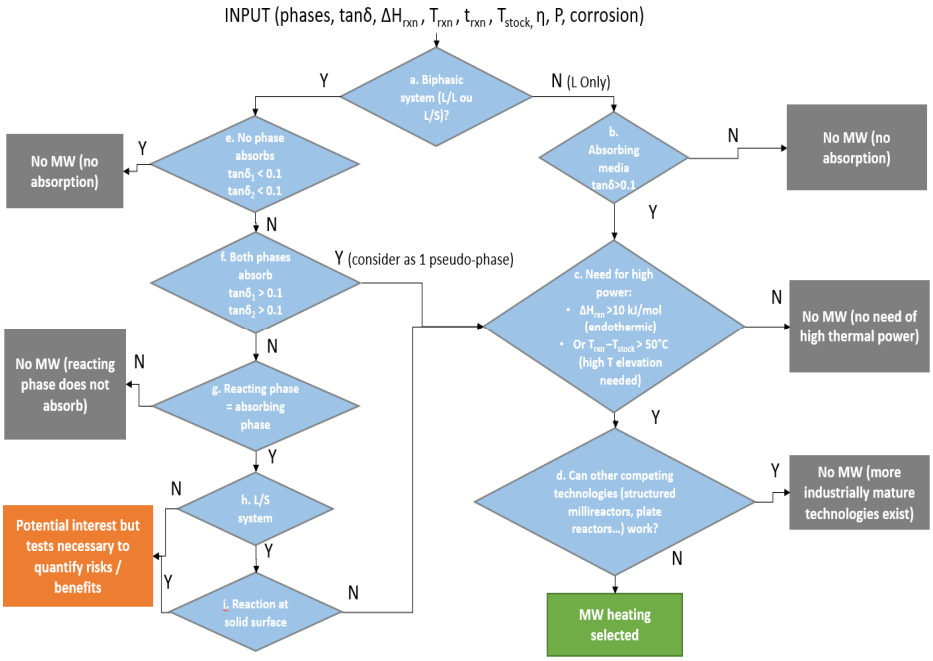

Fig. 1. Methodology for helping into the selection of microwave heating for organic reactions

The flowchart can be divided into two sections:

- Single-phase liquid case (right section)
- Multiphase case L/L or L/S (left section)

For the single-phase liquid case, the criteria that should be met to retain microwaves heating as an advantageous technology compared to the existing ones are:

- A need for high heating power (endothermic reaction or high temperature reaction)
- Difficult heat transfer from the walls (eg. high viscosity, thick walls due to pressure constraints, poorly conducting materials due to chemical compatibility constraints,…)
- Competing technologies not applicable (high solid content, fouling risk…)

For multiphase case the reacting phase should be the absorbing one (if both phases absorb then the media can be considered as a single pseudo-phase). This being true, two scenarios are possible:

- L/L system or L/S system with reaction at solid surface: the use of microwaves could be advantageous if, for any reason, a thermal gradient between the two phases could be maintained, and this would have a positive effect on the reaction performance (lower energy consumption, increased selectivity, accelerated
- material transfer processes, local overheating at the reaction site and consequent acceleration of the kinetics...). On the other hand, it is important to be able to control this thermal gradient and avoid local runaway. It is very difficult to predict this type of situation ‘a priori’: more detailed work (experimental and/or simulation) is needed to quantify benefits and risks.
- L/S system with reaction in the liquid phase: the solid is then an inert or a reactant that dissolves or a product that precipitates. The potential benefits of microwaves are related to the heating of the reaction liquid phase

Kilolab microwave reactor for data acquisition

The main particularity of integrating microwave reaction in our panel of technologies is that, due to the lack of industrially scalable tools, Processium developed its own pilot scale equipment. This consists in a new microwave irradiated stirred tank reactor [[5]] based on the INTLI technology developed by Sairem [[6]] having the following characteristics:

- 1L volume
- Equipped with double jacket, allowing direct comparison between different heating modes
- Capable of working at high T and P (250°C, 40 bar)
- Working in batch mode or continuous mode up to 20 L/h
- Built in non-transparent microwave materials (metals) thanks to the INTLI technology
- With close-to-ideal hydrodynamics (fig. 3)
- With perfectly characterized heat balance

Fig. 2. Microwave reactor and generator

These characteristics have been defined in order to be able to propose an experimental tool:

- Working under a wide range of industrial conditions (high temperature and pressure)
- Allowing the scale up of the results with the classic methods of chemical reaction engineering coupled with electromagnetic simulation for industrial detailed design
- Adapted to acquisition of intrinsic chemical kinetics, without biases coming from microwave related reasons (poor temperature measurement, heterogeneous temperature distribution, value of power absorbed by the media poorly known…)

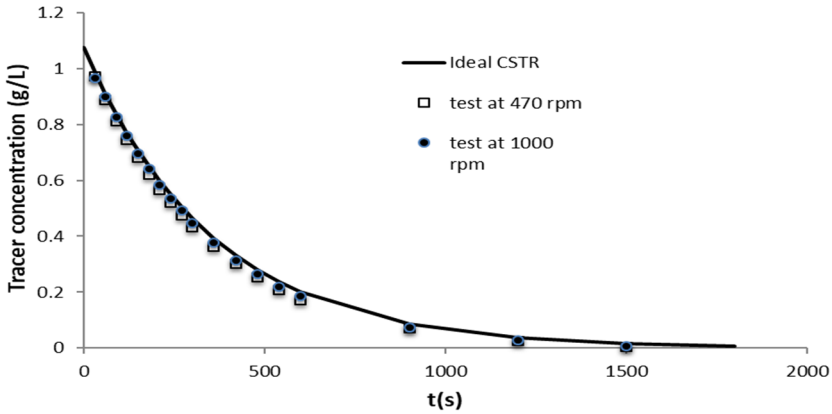

Fig. 3. RTD of the reactor at different stirrer speeds compared to an ideal CSTR

By establishing a detailed heat balance on the reactor and after few experiments having the objective to determine the model parameters (heat transfer coefficients and inert heat capacity – Table 1) it is possible, since SAIREM generator indicates continuously incident and reflected power, to know with precision at each instant the heat lost to the environment and the power used to heat up inert metal mass.

Table 1. Values of heat transfer coefficients calculated from experimental characterization

Heated liquid	Max MO power (kW)	T (°C)	P (bar)	U (W/m²/K)	U losses (W/m²/K)
Ethylene glycol	2	180	10	908	70
Water	1	80	1	777	69
Water	2	150	7	1027	53
Water	2	80	1	1222	48

This leads to a good knowledge of the microwave power effectively absorbed by the reaction media.
Fig. 4 shows an example of a measurement of power effectively absorbed for a liquid heated up to 150°C. It is visible how the power effectively absorbed by the liquid media is a fraction of the microwave power produced by the generator and how it's possible to follow its evolution with time. This methodology allows then to know the real power absorbed by the media, per unit of mass, which has to be kept constant during scaleup.

Remark: noise visible in the next figure comes from noise in temperature measurement (+/-1°C) and power measurement (+/-20W), which are amplified by calculations.

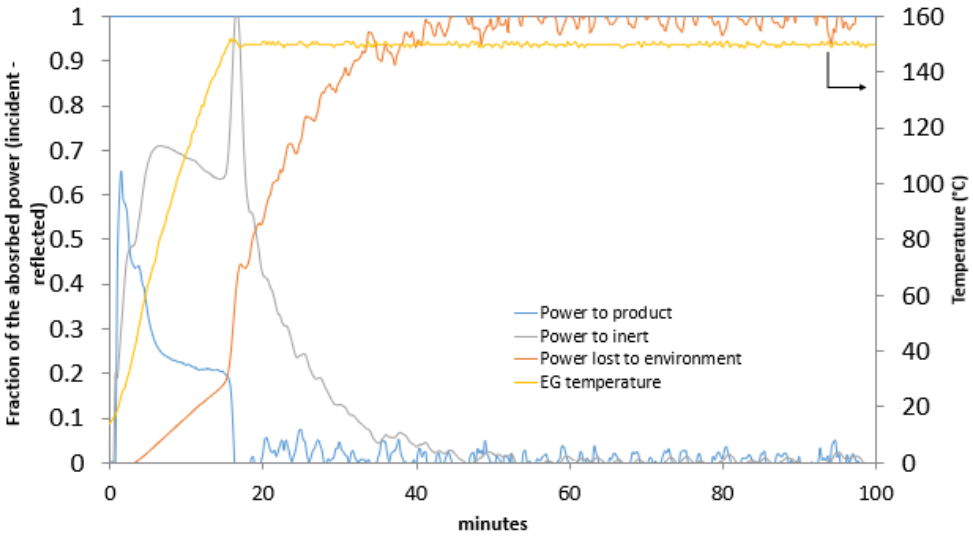

Fig. 4. Example of detailed calculation on microwaves power effectively absorbed by the heated product during a batch test

Two versions of the experimental setup are available, differing by the material of the part filling the gap between the tank and INTLI. This part should ensure sealing while being transparent to microwaves:

- Teflon version: experimentally tested with success up to 200°C and 20 bar, point at which Teflon starts to deform
- Ceramic version: work ongoing to identify the most suitable material, alumina and other ceramics being unsuccessfully tested (brittleness problems)

Example of reaction intensification and industrial projection

The experimental tool presented in the previous paragraphs is then suitable to be used to acquire fundamental data on intrinsic reaction kinetics under microwave irradiation. Kinetic models built on measured data are then used to size industrial reactors or to identify operating conditions optimizing the reaction performances. The following example shows how this work is conducted on a reaction of industrial interest

Production of molecule of interest via an acetylation is conducted industrially in batch mode in a few m^3 reactor at 80°C. Yield is quite good (96%) but byproducts are highly fouling and are responsible for malfunctions in the purification section. A new synthesis path has been discovered which does not produce fouling byproducts but shows poor performances at 80°C (49% yield of main product).

Microwave reactor is then used to measure kinetics and performance of the reaction at different conditions. Results are presented in Fig. 5.

It is important to note that results obtained under classic heating (by the customer at 80°C, or during this study at 110°C) are really close to the ones obtained under microware heating at the same temperature, meaning that:

- No specific microwave heating effect is measured
- The equipment can effectively be used to compare directly the performance of different heating modes

This being said, one can notice from Fig. 5. that yield is improved by conducting the reaction at high temperature and low residence time.

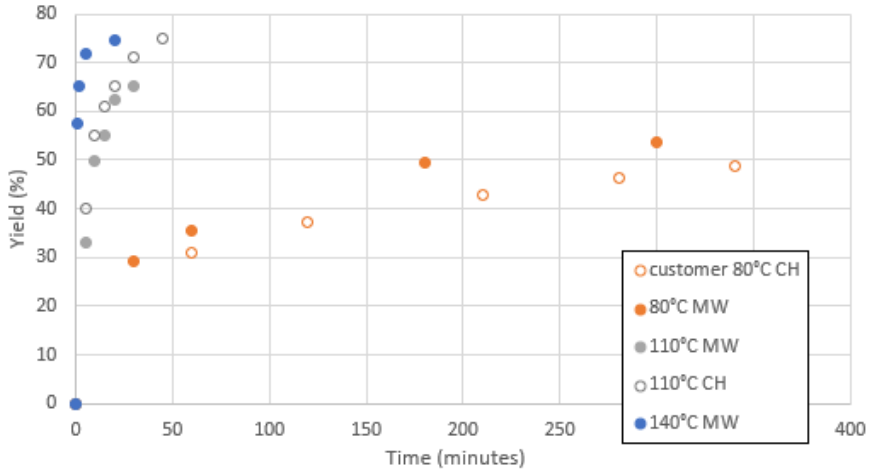

Fig. 5. Yield vs time for different batch trials; MW = microwave heating, CH = classic heating

A kinetic model has been developed based on these experimental data and used to predict optimal product yield at higher temperature. For each temperature, the volume of a theoretical continuous stirred tank industrial reactor is calculated. Effective microwaves power needed to heat the feed from room temperature to reaction temperature is also estimated. Basis for the calculations is a production of 520 tons per year of product of interest. Results are given in Table 2.
Please note that extrapolation of kinetic models outside experimental range should always be verified by experiments afterwards. In this case the work shown here is purely demonstrative.

Table 2. Theoretical reactor presizing as a function of reactor temperature

T (°C)	Optimal res time (s)	Optimal yield (%)	Industrial reactor volume (L)	MW power absorbed by product (kW)
110	4714	41.9	394.2	15.1
150	658	52.4	43.9	17.4
200	86	62.7	4.8	20.1
250	17	70.0	0.9	23.0

Working at high temperature favors the yield in product of interest. This, coupled to the relatively small size of the industrial reactor necessary to ensure the desired production, suggests that microwaves heating could be advantageous to apply industrially for this example.

Conclusions, limitations and future work

The key to our vision is to treat microwave technology as a simple (but particular) means of heating and take the necessary precautions to be able to scale-up with conventional chemical engineering tools. Different approaches are used together to achieve this objective:

- Development of a methodology to help in microwave technology selection since the early stages
- Development of an experimental technology to acquire key data for microwave reactor sizing
- Modeling and sizing using classic tools of chemical engineering

Two main axes for future work and improvements are identified:

- Improving the reliability of the experimental tool by identifying the right ceramic material that would allow working at higher temperature and pressure
- Include electromagnetic modeling during the industrial reactor sizing step

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