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Microwaves under pressure for the continuous production of quinoline from glycerol

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ABSTRACT

Microwave heating is an interesting technology for chemical engineering, since it can provide effective volumetric heating of the reaction medium and reduce energy costs. Many commercially available laboratory-scale microwave reactors have already been used to carry out chemical reactions on a small scale (a few milliliters), and at high temperatures and pressures. Some research has been undertaken to scale-up microwave processes and make them suitable for a larger scale production.

Indeed, combining wave propagation through the walls of a reactor with resistance toward high pressure and temperature as well, is not an easy task. For these reasons, this work focuses on the development of a pilot scale microwave apparatus used for the heating of larger reaction volumes under pressure, and under controlled conditions. The specially designed microwave apparatus allows chemical reactions in batch or continuous mode. The applicator operates in single mode enabling a uniform electromagnetic field, and well controlled operating conditions. The main advantage of the setup is the quite large reactor volume that permits either relatively long residence times or relatively high mass flowrates (up to 1 kg/h). The developed microwave apparatus was then used for quinoline synthesis from glycerol via a modified Skraup reaction. The major advantage of our system is the ability to carry out continuous chemical synthesis, at a large pilot scale, and high temperatures (200–220 °C), while ensuring a better control of the pressure (max. 19 bar) through the control of the power absorbed by the reaction medium.

1. Introduction

The application of alternative forms of energy sources for conducting chemical reactions is at the heart of process intensification approach. Among these energy sources, microwave heating is recognized as a very promising technique to intensify chemical processes [1,2]. One can notice the rapid growth of microwave assisted procedures in organic synthesis since the publication of the pioneering papers by Gedye et al. [3] and Giguere et al. [4] in 1986. Rapid microwave protocols can be developed for most chemical transformations requiring heat. The activity in this new technique has experienced exponential growth and has been reviewed in the areas of material science, food technology, environmental technology, organic synthesis, polymer synthesis, etc. [5,6]. Indeed, microwave technology is already used in some industrial sectors such as in the drying process of fruits, food, and pharmaceutical powders as well as for polymer chemistry. In medicine, microwaves are used in resonance therapy and thermography [7,8]. Microwave irradiation offers many advantages compared to conventional heating. Electromagnetic energy is actually transferred directly into the material via radiation without loss by means of heat conduction and convection. Consequently, an instantaneous and uniform volumetric heating is obtained for microwave-absorbing material, and heating occurs therefore from the inside to the outside of the medium. Easy automation and incident power control are also achieved. In numerous chemical syntheses, rapid heating, selective heating and enhancements of yield and purity are obtained [5,8,9].

Many laboratory-scale microwave reactors have been widely used for conducting different chemical reactions. The commercially available microwave devices are divided into two groups. The first category consists in multimode ovens. They are often equipped with a small tubular reactor inside (Teflon coil, or glass or quartz tube) [10], of only a few milliliters, in which different organic syntheses have been carried out. Some of them have been performed under high pressure (up to 120 bar) and at temperatures of up to

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250 °C [11,12]. Most of the devices have been optimized in order to achieve better reaction control, namely temperature and pressure control. These developments have obviously led to investigating the scalability of microwave heating, either by using larger reaction volumes in batch mode, or by multiplying the number of small vials in the ovens [12–15], or by using the continuous mode [16–18]. Despite being able to control the main parameters (temperature, pressure, and reaction medium stirring), as well as the automation of the device, an important parameter remains uncontrolled: the electromagnetic field distribution. While most of the commercially available multimode devices involve a static microwave diffuser to homogenize the wave distribution, the electromagnetic field distribution can never be controlled and its homogeneity cannot be ensured. This leads to a lack of temperature uniformity in the reaction medium and hot spots can occur, especially if the cavity possesses multi-reaction vials.

The second category consists in more advanced microwave reactors, involving a waveguide to create a standing wave. Single-mode applicators are used, allowing the propagation of a quasi-uniform field on the reactor zone. The reaction can then be conducted under well controlled operating conditions. The electric field densities in single-mode cavities are higher, allowing absorbing mixtures to be rapidly heated. Microwave input and reflected powers can be measured, the absorbed energy estimated, and the interactions of the wave with the medium can be identified. The most commonly used batch devices (e.g., Biotage, CEM, Anton Paar) permit, in some cases, interesting conditions for chemical reactions (temperatures up to 300 °C and pressures up to 30 bar). However, in these commercially available single-mode batch reactors, the reaction volume is very small (∼50 mL) and not adapted to production [19,20].

As for multimode systems, some studies have focused on the scalability of single-mode pressurized devices, either by allowing larger volume reactions (12 bar, 500 mL)[21], or by developing continuous mode tubular reactors [19,22,23]. Although these developments have led to conducting chemical reactions at high temperatures (up to 300 °C) and under pressure (up to 50 bar) [19], once again, the volumes do not exceed 50 mL. This lays down typically short reaction times (in the order of a few minutes), and small flow rates. Despite these improvements, there are many remaining difficulties to scale up microwave pressurized reactors. One of the main limitations is the restricted penetration depth of microwave irradiation into absorbing materials, which is generally in the order of just a few centimeters. When using larger batch reactors, reagents in the center of the reaction vessel are mostly heated by convection and not by direct microwave dielectric heating. The heating rate of the mixture is therefore affected, leading to extended processing times [20,24]. This physical limitation is one of the main reasons for the development of continuous flow reactors.

Another important issue for the scalability of the continuous pressurized microwave reactions is the necessity to use reactors that are transparent to microwave. Only materials like quartz glass, some polymers and some ceramics can be used [19]. However, combining these materials with resistance toward chemicals, high pressure and temperature is not easy to carry out. Thus, scaling-up microwaves must mainly fulfill the following criteria: (1) safe and reliable equipment, (2) high reproducibility, (3) good reaction control, (4) fast heating time, (5) reasonable volume, (6) acceptable energy balance, (7) comparable or higher yield to conventional systems, and (8) acceptable cost [19].

Keeping these issues in mind, the challenge of this work is to design a continuous microwave reactor dedicated to organic synthesis at high temperatures and pressures. A chemical production of about 1 kg/h is targeted, for relatively slow reactions requiring quite long residence times (10–20 min). This device has to operate reliably and safely with volatile compounds including organic solvents. Nevertheless, developing a microwave-transparent reactor with resistance toward pressure is a hard task. Indeed, controlling experimental conditions has to be managed, including pressure, temperature, time, homogenization of the medium, reagents/products flow (in the case of continuous mode reaction), and post-reaction cooling. Our approach requires scale-up, solving the technical issues, in terms of technical tools for temperature and pressure measurement and control, as well as reactor design and implementation of elements allowing batch and continuous mode operations for larger quantities. It is also imperative to ensure that the apparatus functions safely, and to plan power control and anticipate intervention procedures in the case of any emergency.

The developed microwave pilot has been tested on quinoline production from glycerol using a modified Skraup reaction. This reaction is of great interest for the production of a pharmaceutical intermediate (quinoline) from a biosourced material, glycerol. In a previous study [26], we demonstrated the feasibility of the reaction under microwave irradiation in green conditions, using water as a solvent and sulphuric acid as a catalyst, without any additional oxidant or toxic reactant. High temperature (220 °C) and pressure (15–25 bar) are required for the reaction. Acrolein is produced as an intermediate, and reacts in situ with aniline to produce quinoline, therefore avoiding handling with its toxicity and instability. The developed microwave pilot was operated for quinoline production in both batch and continuous flow modes and temperature/pressure/power control were ensured.

2. Batch mode

Our team has been investigating microwave synthesis of quinolines for several years, using a laboratory scale apparatus (monowave 300 from Anton-Paar), where a few milliliters (30 mL) of reagents were used [25,26]. In this small apparatus, the Skraup reaction was performed starting from glycerol (30 mmol), aniline (10 mmol) in the presence of sulphuric acid (30 mmol) in 10 mL of water, under microwave irradiation, at 220 °C (25 bar pressure) for 10 min, giving quinoline with a 44% yield. We decided first, to increase fivefold the reactor volume in order to check the feasibility of the reaction at a larger scale, focusing on the good propagation and absorption of the electromagnetic energy in the larger volume. We also wanted to develop a reactor volume more compatible with a 1 kg/h continuous production of quinoline.

2.1. Microwave apparatus

The cylindrical PTFE reactor was designed and customized, allowing reaction volumes up to about 135 mL, that is to say, five time more than the reacting volume used for our first investigations [25,26]. The temperature inside the reactor was measured using an optical fiber immersed in the reaction medium through a glass tube. The complete batch experimental diagram is shown in Fig. 1. Our system consisted of a Sairem (GMP 20K/SM) microwave high-voltage generator providing power up to 1900 W, coupled with a magnetron delivering an electromagnetic wave at 2.45 GHz. Only incident and reflected powers were measured with power sensors and the absorbed power was deduced from the difference. The magnetron was connected to a WR340 waveguide allowing stationary waves propagation in a TE10 mode. A tuning piston at the end of the waveguide was used to optimize the electromagnetic energy absorption by varying the guide length. The waveguide was equipped with an applicator and a chimney in which the reactor was inserted. Pressure control was assured by elements installed downstream to the reactor: a pressure sensor, a safety valve (calibrated at 25 bar), a pressure regulator equipped with a gauge and a valve. Computer control and supervision of the set-up were carried out using Labview software.