Microwave Miniature Coaxial Reactors for On-Demand Material Synthesis

Guennadi Kouzaev [1] and Sergey Kapranov [2]

[1]Dept. of Electronic Systems
[2]Affiliation not available

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Abstract

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Guennadi A. Kouzaev
Department of Electronic Systems
Norwegian University of Science and Technology, NTNU
7491 Trondheim, Norway
E-Mail: guennadi.kouzaev@ntnu.no

Sergey V. Kapranov
Moscow Representative Office of A.O.Kovalevsky Institute of Biology of the Southern Seas of Russian Academy of Sciences
119334 Moscow, Russia
E-Mail: sergey.v.kapranov@yandex.ru

***Abstract*—In this contribution, microwave-assisted heating of reference alcohols in miniature coaxial waveguide reactors is studied both experimentally and in simulations. The advantages and disadvantages of heating in the coaxial reactors are considered, and the techniques of coaxial waveguide reactor improvements are proposed.**

Keywords—microwave heating, microwave-assisted chemistry, coaxial reactors

I. Introduction

Today, increased attention is paid to development of miniature, computer-controlled chemical hardware for rapid manufacture of materials and pharmaceuticals on demand with minimal involvement of operating staff [1-3]. The technology is promising for point-of-use manufacturing, including that in remote areas and on future space stations. It is especially interesting to use microwave-assisted chemical reactors for rapid synthesis of materials [4,5]. In many cases, this allows accelerating the chemical reactions on account of enhanced thermal inflow and, probably, non-conventional mechanisms, which are still debated in the scientific community. For instance, in a recent paper [6] an essential increase of chemical rate and yield in microfluidic reactors heated by microwaves in comparison with the conventionally heated ones was observed.

There are many reactor types reported in literature and used in research laboratories and industry. Typically, they are large microwave ovens with embedded vessels for standing-liquid and continuous-flow chemistry. To enhance the yield, increased pressure is applied, preventing boiling at high temperatures. The hollow-cavity reactors are difficult to miniaturize due to low frequencies used for penetrating the volumes of lossy liquids. Some reactors are just hollow waveguides whose cross-section is large enough to support excitation of microwaves at industrial frequencies.

Miniature integrated transmission line reactors can be adjusted to registering local voltages by computer using an analog-to-digital converter. They can be excited by GaAs or GaN microchip generators with the power up to several kW [7,8], but these reactors require additional heavy shielding preventing the life-threatening radiation leakage into the environment. The hollow coaxial waveguides in microwave-assisted heating and chemistry are considered in [9-12]. This sort of waveguides allows being scaled down and up because it supports the transversal electromagnetic (TEM) mode [9, 13], and it can be used even in its nanoform [14] to handle dipolar molecules for electronically-controlled molecular interactions and, in the future, for nano-chemical processes. Another promising feature of coaxial reactors is that their main TEM mode has no cut-off frequency and the frequency-sweeping techniques can be used to avoid the problems of high-frequency penetration [15].

This abstract describes the microwave hardware, reactors, and some results of the experimental study of liquid heating in miniature coaxial vessels. The obtained results and techniques are prospective for future experimentation and developments in microwave-assisted chemistry and pharmacy.

II. Coaxial Reactor Design and Microwave Hardware Used

One of the studied coaxial reactors is shown in Fig. 1. It is mounted inside a box (1) that allows studying the reactors of different geometry. The reactor (2) is connected to a microwave generator KU SG 2.45-25A from Kuhne Electronic GmbH (Germany) and the 50-Ohm load using the coaxial connectors (3) and (4).

A liquid is pumped inside and evacuated outside through copper tubes (5) and (6) soldered to the coaxial body with a high-temperature silver solder. To reduce the cost of the experimental setup, the copper tubes used are made from RG402 (reactor body of the length 48 mm) and RG405 (inlet and outlet tubes) although other types of the coaxial waveguide can be used with appropriate connectors. The central silvered copper conductor is from RG402 waveguide as well, and the PTFE inserts (with length 25 mm each) of the mentioned waveguide support it. These inserts are tightened well so as to not allow liquid leakage during the experimentation with methanol and ethanol pumped inside the reactor using a syringe pump NE-300 from New Era Pump Systems Inc. (USA).

To ensure the electromagnetic (EM) safety of experiments, the connectors should be tightened up well enough; the inlet and outlet tubes should be long enough (20 mm) to not allow non-propagating modes of circular waveguides of very small diameters, such as that of RG405 waveguide outer shield, to

reach the ends of the tubes. To verify the EM safety, the possible parasitic radiation is controlled with a microwave indicator Voltcraft WT-2G. All experiments are performed at 2.45 GHz of the 10-W power controlled with a power meter Anritsu ML2438A at the generator's input and a reflected wave indicator.

The temperature is measured with thermocouples from Omega Engineering. For this purpose, two of them are used one by one in successive experiments for verifying the reliability of measurements: TC1 stands for probe 5SC-TT-K-30-36, and TC2 denotes model KMTSS-IM025G-150. The results of temperature measurements are processed by an electronic module UTC-USB (Omega Engineering) with the measurement discreteness of 1 °C and are stored in a computer. The probes are installed inside tubes (3) or (4) close to the openings where the microwave field is minimal and does not distort the probe readings.

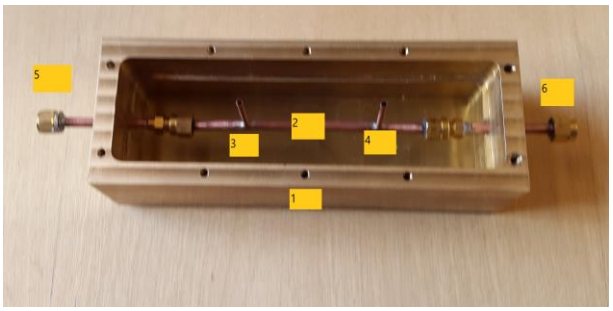

Fig. 1. The coaxial reactor in a universal setup. See comments in the text.

III. Experimental Results and Their Analysis

Some experimental results for heating methanol (Merck, >99.9% purity) and absolute ethanol (Arcus produkter AS, Oslo) are shown below in Figs. 2 and 3, respectively.

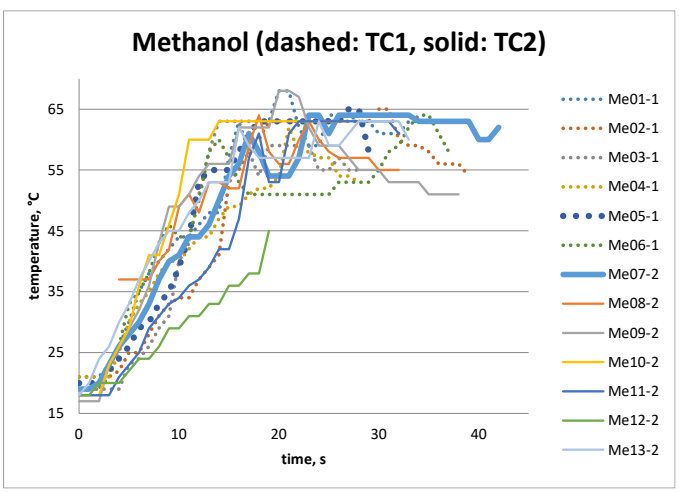

Fig. 2. Temperature trends of methanol heating in the coaxial reactor (standing liquid regime; the reactor is in the vertical position). Thermocouple sensors TC1 and TC2 are inserted through the tube (3) close to the generator port.

It is seen that the readings of the two sensors TC1 and TC2 are close to each other although the temperature trends show fairly turbulent heating dynamics. It is explained by the fact that the studied alcohols are very lossy substances and the microwave field decreases fast in the direction away from the exciting port (Fig. 4), thus creating considerable temperature and density gradients. This electric field distribution is obtained using COMSOL Multiphysics Simulator [16] on an assumption of the weak-field excitation of the reactor.

Then, the heating of liquids is due to the turbulent flow along the reactors and heat transfer along the conductors and liquids. The air convection around the tube plays an essential role in randomization of the temperature trends, and usually, use of external polymeric thermal insulation on the miniature reactors leads to smoothening of the curves.

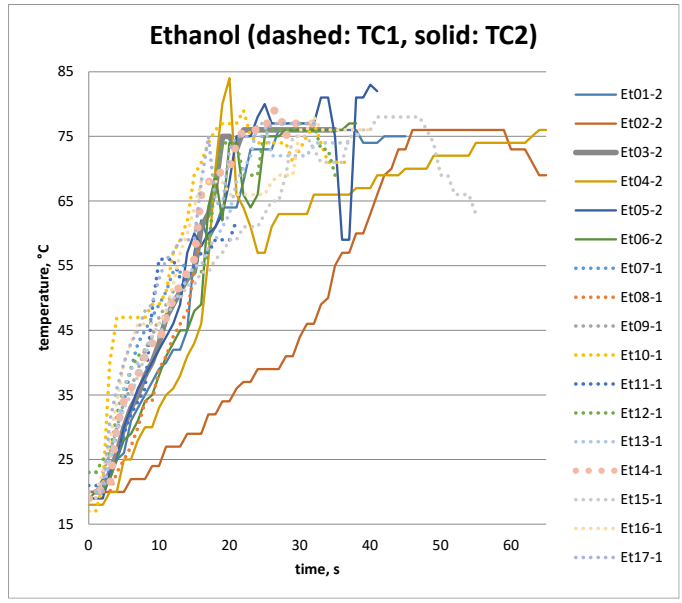

Fig. 3. Temperature trends of ethanol heating in the coaxial reactor (standing liquid regime; the reactor is in the vertical position). Thermocouple sensors TC1 and TC2 are inserted through the tube (3) close to the generator port.

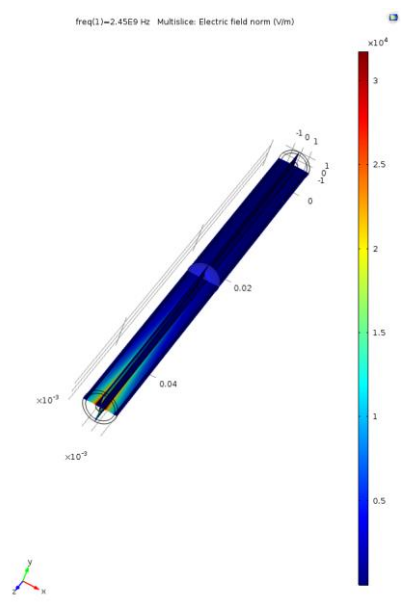

Fig. 4. Microwave (2.45 GHz) electric field distribution in the methanol-filled coaxial reactor at 20 °C calculated with Comsol Mutliphysics. Relative complex permittivity of methanol at this frequency and temperature is $\tilde{\varepsilon} = (20.6, -13.95)$, see [8].

This turbulent pattern of heating of static liquids may constrain the use of coaxial reactors in chemistry, but continuous-flow reactors are less sensitive towards the longitudinal locality of heating. More homogeneous temperature distribution can be achieved by thermal insulation of reactors, using less polar solvents, and using frequency-sweeping generators [15].

Most important is the prevention of bubbling (seen in Figs. 2 and 3) which can be realized by pressurizing the reactor contents for elevating the boiling temperature. The cross-sectional uniformity of temperature deteriorates with the diameter increase, and it is improved by using the multiple-wire designs [9], dielectric and high-resistivity inserts [9,11], intensive ultrasonication [9], and liquid mixing [10].

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