Industrial Microwave Applications

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***Abstract*— This paper presents the versatility of microwave industrial applications giving examples of the experience at the Microwave Laboratory of IMT in the development of microwave assisted process equipment. Some previews of possible future evolution of this branch of the use of microwaves are also presented.**

***Index Terms*— Industrial microwave applications, microwave chemical reactors, microwave chemistry, microwave heating equipment.)**

I. INTRODUCTION

The study of industrial microwave applications at the Mauá Institute of Technology (IMT), began in 1968, with research grants from the Research Foundation of the State of São Paulo (FAPESP). On the occasion of the founding of SBMO in 1982, several industrial processes had been already studied in the IMT Microwave Laboratory (LMO), mostly by request of local industries. High-power microwave generators were very expensive and difficult to import, so applicators with a modular design [1] were developed and the required amount of RF power were obtained with domestic oven model magnetrons.

In 1994, when the Brazilian National Research Council (CNPq) Research Group Directory was established, the Microwave Applications in Chemical Processes Group was created, being active to this day. In 2006, LMO participated in the stricto sensu graduate program in Chemical and Biochemical Process Engineering of the then newly created IMT University Center (CEUN-IMT), supporting the development of twenty-eight master's theses, twenty-five in the area of microwave applications to chemical processes and three in the area of industrial applications of electromagnetism. Previously, microwave experimental work performed at LMO was used for Master and Doctor degrees from the University of São Paulo – USP – obtained by LMO collaborators. Along these 54 years of work, several processes equipment were developed, from oven dryers to continuous microwave-irradiated reactors used in various processes, from banana oil extraction to the production of green ethylene. Part of these results has been patented, generating thirteen patents so far. Methods of characterization of dielectric materials also were developed.

On the following sections, there is a brief presentation of the projects carried out by the LMO.

II. CHEMICAL, PETROCHEMICAL AND FOOD INDUSTRY

All of them are chemical processing industries distinguished by the nature of the raw material, operating temperature range and requirements for different quality levels. Its processing falls into two fundamental concepts: unit operations and unit processes.

A. Microwave Assited Unit Operations

For unit operations when dealing with microwaves a fundamental issue is its dielectric heating mechanism, which has the advantage of homogeneous and rapid volumetric heating, with media dependence. A drying operation was first demonstrated at the annual meetings of the Brazilian Society for the Progress of Science (SBPC) in 1978 and 1979 [1] with a prototype of a continuous microwave oven with a conveyor belt (1.5 m length and 0.15 m width) and two periodic structures acting as filters. Further development led to the design and construction of a continuous belt oven (5.0 m length and 0.3 m width) (Fig. 1) with 12 kW RF power. Among the projects carried out in this oven were the drying of gypsum molds [3] used in the ceramic industry after de-molding the ceramic piece in green (wet) and the drying of iron ore [2]. A second bench-scale continuous belt oven (1.5 m length and 0.2 m width) with 6 kW RF power was designed and built; drying of residual sludge from urban effluent treatment plants [2], chemical industrial plants [4, 5], automotive paint lines [6], and the study of soybean drying [7] for silage were investigated with this prototype, proving its feasibility. In a batch oven, the feasibility of drying acrylic paint for road signaling was studied [8]. A traditional “cubic” batch oven was improved with a two-port cavity and pyramidal waveguide transitions geometry; a semi-analytical scale coupled to it allowed continuous measurement. This equipment was used to study drying processes of ceramic fiber [3], bauxite [3], aluminum dioxide [3], calcium carbonate [9], and magnesium sulfate [10]. The phenomenon of overdrying through microwaves was studied [10]; it occurs when water is removed not only lowering moisture but also from the molecular constitution [11].

Fig. 1. Continuous microwave belt oven. Inset shows the dried iron ore at the output.

An evaporator was developed for the recovery of ammonia from solutions of heavy metal chelates [3]; microwave radiation occurred through a window aperture. It has the advantage of avoiding deposits of these salts on the conventional heat source surface. A waveguide-coaxial transition was used to implement an immersed-antenna within a continuous evaporator for concentration of saline solutions [12] and to serve as a reboiler for distillation columns (Fig. 2) of heavy products in the oil and petrochemical industry [13].

Fig. 2. Thermography of distillation column reboiler pilot in operation.

Liquid substrates offer a wide range of microwave applications as an energy alternative option. They include solvent extraction of oil from banana [3], pasteurization of coconut water [14], pasteurization of peach palm pappardelle packed in polyethylene bags [15], starch gelling for gummy bears [3]. In the food segment, microwave-irradiated cooking process of instant noodles [3] and various aspects of microwave popcorn preparation [3] were also studied.

The design of more efficient applicators will be a trend in the process equipment industry to take advantage of the versatility of microwave heating.

B. *Microwave Assisted Processes (Microwave Chemistry)*

When considering unit processes associated with microwaves then the most important effects on chemical reactions are characterized by its acceleration and the influence on the purity and yield of the synthesized products. When there is no evidence of interaction (of the electromagnetic energy) on the reaction mechanism, then the reaction is said to be assisted by microwaves; the opposite is said to be stimulated by microwaves. An example is the preparation of octyl maleate by the esterification of maleic anhydride (MA) with 2-ethylhexanol alcohol (EHO) with p-toluene sulfonic acid (PTSA) as a catalyst: the reaction under microwave irradiation is faster than the Synthesis with electric heating [16] (FAPESP Grant 2001/13299-0) when compared to the same conditions of temperature, agitation and composition of the reagent medium. Relevant kinetic equations were determined in a conventional heating reactor and also in a thermostatized microwave reactor (Fig. 3); the results in Table I demonstrate the effect of the RF energy on the reaction mechanism as seen in the changes of the values of the kinetics parameters. They also indicate synergy between acid and microwave catalysts [17], as long as the phenomenon is both sensitive to the acid concentration and to the applied RF power value.

Considering industrial conditions, these results have potential to transform slow reactions in fast ones [18] by judicious adjustment of catalyst and microwave power levels. This is a new application of microwave chemistry, having potential to improve flow chemistry processes [19]. Flow Chemistry issues show a tendency towards microwaves; it will help the future of the chemical industry, both in commodities and chemical specialties.

Fig. 3. Thermo-controlled reactor in a pyramidal cavity.

TABLE I

Kinetic equation of maleic anhydride esterification with 2-ethyhexanol

$$-r_{MA} = k_0 \exp\left(-\frac{E}{RT}\right) c_{MA}{}^{n_{MA}}\, c_{EHo}{}^{n_{EHO}}$$

Kind of heating	PTSA concentration (M)	k_0	E (kcal/mol)	n_{MA}	n_{EHO}
electrical	---	2.29e+78	149.32	0.89	2.47
electrical	0.006	1.39e+25	46.30	0.56	2.18
electrical	0.012	2.96e+8	15.87	0.25	0.65
microwave	---	6.66e+14	25.65	1.59	2.25
microwave	0.006	6.90e+21	40.73	1.04	1.98
microwave	0.012	2.36e+52	19.31	0.25	0.05

Studies were carried out using microwaves in the production processes of aspirin [20, 21], di-octyl phthalate [22, 23], monobutyrin [3], aldolization of heavy aldehydes [3], and synThesis of ε-caprolactam [24]. Other studies were in polymerization processes such as the preparation of polystyrene [25], orthophthalic polyester resin [26], styrene acrylic resin [3], rubber vulcanization [3], manufacture of polyurethane foam pillows [3], and sawdust composite with urea-formaldehyde resin [27-29] and epoxy resin curing for finishing granite stones [3]. A mobile microwave applicator with a horn antenna was developed to accelerate the curing of epoxy resin for repairing cracks in asphalt road pavement [30]; this work won the 2009 Award from the Regional Council of Chemistry, Brazilian IV Region (CRQ IV).

In the environmental area, studies were carried out to eliminate pollutants in sewage by the action of hydrogen peroxide under microwave irradiation for the decomposition of phenol [31, 32] and for the bleaching of thermomechanical cellulose pulp [3].

Biodiesel synthesis by transesterification of vegetable oils with ethanol was initially studied in a batch reactor and then in a continuous stirred-tank reactor [33, 34]. In the former, the process was optimized by determining the processing conditions (time, power, catalyst, and alcohol/oil ratio) obtaining a yield of 99.2%, which is 1.7 times higher than conventional processes. This optimization won the 2013 CRQ IV Award. Biodiesel was also successfully prepared from soap stocks (vegetable oil purification residue) in a microwave-assisted process, giving rise to a patent [35].

The production of automotive ethanol had two studies. The first was part of a big national project to obtain ethanol from cassava [3]: saccharification of cassava starch was studied and a pilot plant was developed for this purpose [36-39] (Fig. 4). The second dealt with total acid hydrolysis of sugarcane bagasse (FAPESP Grant 2011/50154-9) [40, 41]: a microwave high-pressure semi-continuous reactor was developed to promote the hydrolysis of the crystalline fractions of cellulose that are hardly hydrolyzed. A microwave-assisted hydrolysis of PET resin was also performed [40].

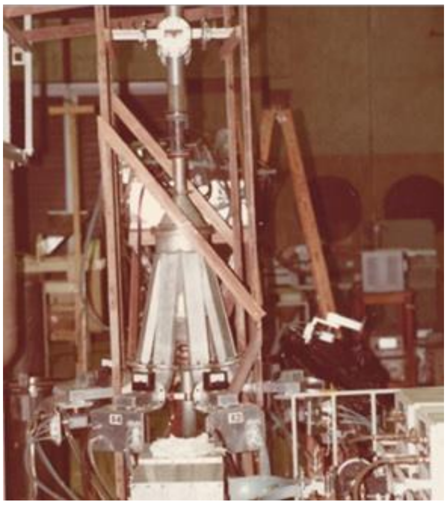


Fig. 4. Microwave assisted cassava saccharification pilot.

The dehydration of ethanol for microwave-assisted production of green ethylene was studied and led to the development of a continuous fixed-bed reactor with a catalyst sensitive to microwave irradiation for its self-heating. A two-port multimodal cavity with pyramidal waveguide transitions was used in this study [43] and 90% yield in ethylene was obtained. This project received a research grant from FAPESP (Grant 2017/24238-7) and two prizes: 2016 CRQ Award and the 2015 Odebrecht Award for Sustainable Development. These results show that microwave-sensitive catalysts are good promises for the chemical industry.

High temperature chemical processes were also studied: cracking of naphtha [44, 45], devolatilization of coal [3], pyrolysis of electronic scrap for metal recovery [46], and resin-reinforced fiberglass for the recovery of glass fibers [47]. A microwave parboiling rice process with a continuous reactor was developed for agro industry sector (Fig. 5) [36].

Fig. 5. Pilot for microwave-assisted rice parboiling.

III. CERAMICS, NANOMATERIALS AND FUNCTIONAL MATERIALS

The dielectric heating capacity of all these materials is fundamental. Direct heating is achieved when the loss factor value permits. Indirect or hybrid heating can also be considered with the use a (second) susceptor to reach high temperatures.

Sintering of transparent porcelain [48] were carried out using a hybrid microwave oven to analyze effects of composition, temperature and sintering time of porcelain with the help of silicon carbide as susceptor. Greater densification of the samples and improvement of dielectric properties [49] in relation to conventional sintering were achieved. Statistical analysis concluded that [50]. there is an observed effect of microwaves on the sintering process of ceramics. It is expected that further investigation and research lead to develop advanced ceramics such as ceramic electrodes and electrolytes for solid oxide, protonic ceramic fuel cells and so on.

Preparation of calcium carbonate with granulometry in the nanometer range was studied via carbonation of calcium chloride solution in a microwave continuous reactor [51]. Microwave-assisted synthesis of ZSM-5 zeolite was also studied to reduce its preparation time and cost [52].

IV. METALLURGY

In metallurgy area of self-reduction of iron ore microwave heating effect get benefit of both permittivity and permeability values of iron ore.

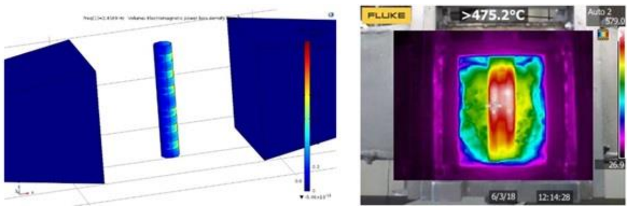
Two FAPESP projects (Grants 2010/51269-1 and 2003/02404-0) were carried out to develop suitable processes and applicators for self-reduction of iron ore pellets. Cubical, hexagonal and cylindrical geometries were studied [53-58]; exploration of results from maximum electric (or magnetic) field amplitude positions, power level, and coupling methods were studied. Cylindrical geometry with a 3-port cavity gave the best response; high energy density was achieved with an adjustable power up to 6 kW (Fig. 6); 100% of the reaction rate was reached in 15 minutes with 90 g of pellets as a load.

Fig. 6. Furnace for self-reducing iron ore pellets. The inset shows the outside surface of the reactor in operation.

V. DEVICES, MEASUREMENT TECHNIQUES AND SIMULATIONS

The operation of high-power microwave heating processes may require the continuous adjusting of the applicator matching as the dielectric properties of the material being irradiated change with temperature. At LMO high-power automatic matching devices [59] and techniques for measuring the variation of complex dielectric constant from room to high temperature were developed for 2.45 GHz and 5.8 GHz applications. [60] is an example of the simultaneous use of both frequencies: one for heating, another for measuring; the interchange of its roles is also possible. Coupling strategy and filtering are very important issues to separate extremely high and low power signals paths inside the structure. This theme was treated in a project granted by FAPESP (Grant 2016/21536-4).

Prior to the popularization of Vector Network Analyzers (VNAs) instrumentation and measurement studies at LMO dealt with theoretical and detailed experimental issues to optimize accuracy of permittivity measurements using resonant cavities [61], modelling coaxial probes used with time domain reflectometers and associated computer data treatment in the frequency domain [62]. Nowadays VNAs, characterization of dielectric properties of materials and full-wave computer simulations are important tools to optimize the processes cited above, especially the geometry details of the devices (cavities and applicators). Figure 7(a) shows a COMSOL Multiphysics simulation results of power loss density in a high-temperature catalytic plug flow reactor and Fig. 7(b) shows the associated thermographic image inside the real reactor in working condition [43].



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