Greening the Green Ethylene with Microwaves

L. A. Jermolovicius*, E. V. S. Pouzada, R. B. do Nascimento, E. R. de Castro, J. T. Senise, B. B. Mente, M. C. Martins, S. M. Yamaguchi, V. C. Sanches

Instituto Mauá de Tecnologia, Laboratório de Micro-ondas (Microwave Laboratory)
Praça Mauá 1, São Caetano do Sul, SP 09580-900, Brazil
* Corresponding author, E-mail: jermolovicius@maua.br

Introduction

Gedye's[1] and Guiguere's[2] papers started a wave of publications on microwave applications to chemical reactions, creating the concept of 'microwave chemistry'. Nowadays, this alternative way to conduct reactions is recognized in the literature (e. g. Smith's book[3], which includes reactions enhanced by microwaves in its chapters, and more than one thousand scientific papers have been published every year reporting experiments on microwave chemistry[4]). These facts show that microwave chemistry is presently accepted as a part of the chemistry's world.

Chemical processing industries are paying more attention to microwave applications in order to enhance chemicals production, which can be confirmed by the number of published patents related to chemical processes enhanced by microwaves[5]. Until the year 2000 only 3.6% of the total of 531 patents in this field were related to microwaves; there was also a boost in these publications since 1996. It is also impressive the fact that, since 2007, the number of publications of microwave applications in chemical processes has grown exponentially.

With the aim of increasing microwave applications to industrial chemical processes a laboratory scale experiment was carried out to stablish the technical viability of producing green ethylene changing the traditional fossil fuel to microwave irradiation as the heat source in its ethanol dehydration process.

Green Ethylene

Ethylene is the most globally produced petrochemical, with a yearly production of 75 million metric tons. It is a raw material used in the production of several petrochemicals including polyethylene brand polymers. The conventional process of ethylene production is the cracking, a controlled pyrolysis, of naphtha or refinery gases. This is an endothermic process, which consumes about of 5,000 kcal/kg ethylene and has 58% yield for ethylene[6]. Energy is supplied by fossil fuel combustion. Due to the historical high cost of petroleum and high production of effluent carbon dioxide, a greenhouse effect gas, there are efforts to develop an alcohol-chemical process for ethylene.

Green ethylene is the same chemical compound, ethene, which is produced by petrochemical route, but its raw material – the ethanol – is a renewable one. Ethanol may be produced from corn, sugar cane, beets, wood or any other cellulosic material. As these sources are renewable, the ethene was named 'green ethylene'.

All these sources are biologically treated in a fermentation process to produce the ethanol, or, more precisely, bio-ethanol. This ethanol is chemically dehydrated to ethene, through a pyrolysis process, as shown in (1). This is a simplified view, because there are 36 different chemical reactions happening simultaneously in parallel and in series[7], most of them producing sub products.

$$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_2{=}CH_2 + H_2O \quad (1)$$

About 278 patents for ethylene production from ethanol were published[5] until 2016, which shows a tendency towards the use of renewable materials instead of petrochemicals ones. For example, in 2010, Braskem, started up a plant to produce 200 thousand metric tons per year[8]. Alumina is the traditional catalyst for this process; however new catalysts have been developed, including several zeolites and metal oxides. Ethylene yield is a function of catalyst structure;

for example, it is 40% for alumina, 50% for cerium oxide, 41% for zeolite HZSM-5, 99.8% for zeolite HM-20[9-11]. This process is indicated in the flowsheet[12] shown in Fig. 1.

Dehydration reaction is endothermic and its energy source is usually fossil fuels. For this reason, the process for green ethylene produces carbon dioxide in the petrochemical process. In other words, the usual process for green ethylene is so pollutant as any other petrochemical process.

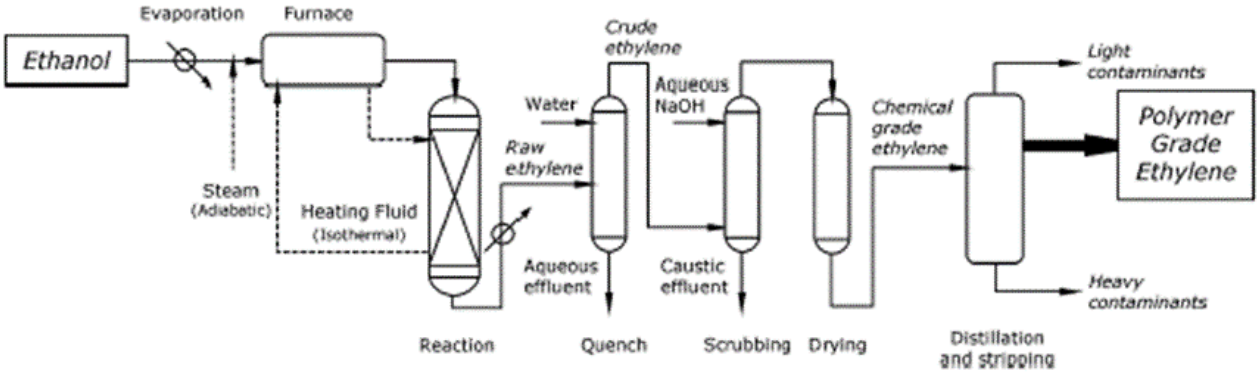

Figure 1: Typical flowsheet for ethylene via ethanol dehydration[12].

Applying microwaves to heat the dehydration reactor was tried in an early work[13]. The idea is to heat the catalytic bed with microwaves, dispensing fossil fuels for this operation and consequently eliminating carbon dioxide generation.

Microwave irradiated flow reactor

A parallelepiped cavity connected to two truncated pyramid waveguides was constructed in aluminum, as shown in Fig. 2. The central parallelepiped section contains the plug flow vapor phase reactor and a cylindrical filter which window allows observation. One side of the cavity is connected to a 3 kW variable-power generator – Richardson model SM 1050D – operating at 2.45 GHz, protected by a circulator, and two directional couplers which allows connection to two power sensors – Agilent models E4419B (power meters) and 8481A (power sensors) – to measure the microwave transmitted power and the reflected power. The difference between measured values is the effective power applied to reaction. At the other side of the cavity, a moving short sets the point of maximum power absorption.

Details of chemical aspects of this reactor are shown in Fig. 3, where (a) is a diaphragm pump (behind the cavity) to pump ethanol from a tank to a vaporizer (b) behind the cavity which receives nitrogen flow through a rotameter (c). Temperature of ethanol vapor and nitrogen mixture is measured by a thermocouple (d). The reactor outlet flow of mixture gases and vapors are collected in a 1 L sample flask (e).

Figure 2: Microwave applicator developed for plug flow vapor phase reactor.

The reaction chamber is a quartz tube with connections: to inlet of ethanol vapor, steam and nitrogen mixture at its top, and to an effluent tube at its bottom. A bed with a ZSM-5 zeolite catalyst sensitive to microwaves is located at middle height of the quartz tube.

The choice of the assembly consisting of the cavity connected to the two truncated pyramid

waveguides was based on multiphysics computer simulation with the aim of obtaining the best possible electromagnetic field distribution around the reaction cavity. Fig. 4 shows a result of the electric and magnetic fields distribution in reactor's cavity.

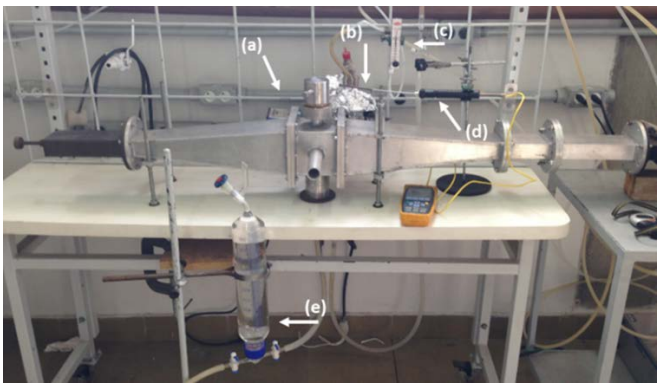

Figure 3: Some details of chemical reactor.

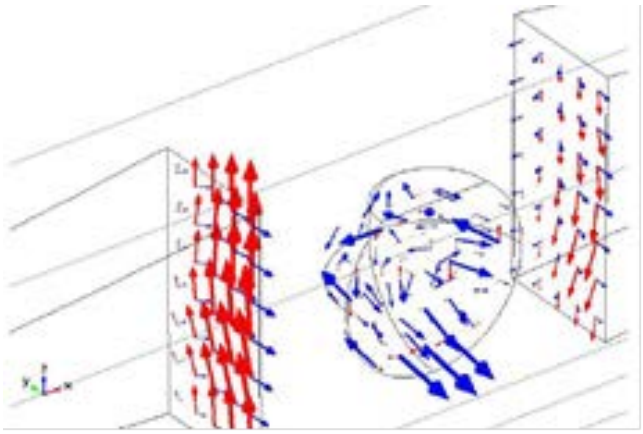

Figure 4: Electric (red) and magnetic (blue) fields simulation for the present cavity.

Microwave assisted ethanol dehydration

Ethanol was boiled in the electrically heated vaporized (b, Fig. 3) and its vapor was dragged with a nitrogen flow. The ethanol used had 12% of water in weight. This mixture was fed to the reaction chamber filled with a mixture of zeolite ZSM-5 pellets and silicon carbide pellets and heated by microwave irradiation reaching 450ºC. Despite of this high value temperature, the cavity surface did not exceed 60–70ºC. The aspect of the heated catalytic bed is shown in Fig. 5. It is a quartz tube with 20 mm diameter and a catalytic bed with 50 mm height. It was also a limiting factor of the whole equipment because this assembly allowed a maximum flow of 2 g/min of ethanol. The effluent product was exhausted from the reaction chamber by natural flow through a discharge pipe which serves the sampling of the produced gases, as shown in Fig. 3.

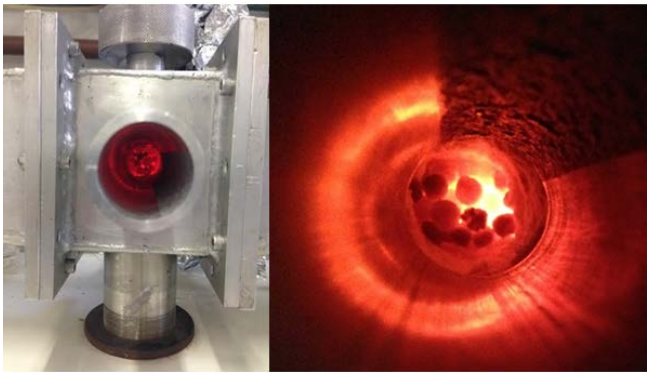

Figure 5: Details of the reaction chamber. (Left): cavity detail of parallel epipedal section, showing the heated catalytic bed. (Right): internal view of the heated catalytic bed.

Table 1. Stoichiometric yield in ethylene (mean value of triplicate tests).

Test	Ethanol concentration (%)	Effective power (W)	Nitrogen flow (mL/min)	Stoichiometric yield (%)
1	78.66	140	220.41	34.7
2	78.66	120	220.41	47.6
3	52.68	130	220.41	32.9
4	70.00	130	138.76	46.1
5	98.87	130	165.95	48.2
6	86.36	113	129.69	48.4
7	87.96	121	172.03	60.8
8	100.00	112	205.30	43.7

Process optimization for laboratory scale reactor

The operation conditions were optimized applying Simplex method[14], for a constant ethanol flow of 1.7 g/min and studying the variables of ethanol concentration (% weight), effective power (W), flow of dry nitrogen (mL/min). The measured variable was the stoichiometric yield of ethylene (%). The tests were done in triplicate. Table 1 shows the evolution of Simplex method; the first four lines are Simplex initial points.

The optimum operation conditions were defined by the seventh point of Simplex, showing the maximum yield in ethylene.

Conclusion

This exploratory experiment demonstrated that it is possible to produce ethylene with microwave-assisted dehydration of ethanol with a yield of 60.8%, in a small-scale laboratory equipment.

The obtained yield of 60.8% is comparable with petrochemical yield of 58%. Comparing it with alcohol-chemical routes[9-11] the obtained ethylene yield is an intermediate result between the minimum (41%) and maximum (99.8%) yield for ethylene that are published. Considering that the test equipment is a prototype under development and that the catalyst may be also optimized, it should be possible to increase the yield in a larger equipment.

Microwaves allow a more rational use of the energy applied to the reactor of dehydration, because only the catalytic bed is heated due to the selective material microwave heating. Consequently, there is no loss of energy in heating unwanted parts of the equipment.

Microwave heating ecological advantage is an important issue due to the suppression of greenhouse gas generation, as it dispenses the burn of fossil fuels to heat the reaction and avoid carbon dioxide generation. These conclusions point out that it is possible to produce a greener ethylene than the actual green ethylene.

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About the Authors

Luiz Alberto Jermolovicius received the B.Sc. degree in chemical engineering from Maua Institute of Technology, and a Doctor degree in chemical engineering from Polytechnic School, University of Sao Paulo. He is a Full Professor at Maua Institute of Technology and was manager of research and development at Elekeiroz S.A. He works in the development of chemical processes and chemical microwave assisted reactors. He is member of ABEQ, ABES and SBMO.

Eduardo Victor dos Santos Pouzada received the B.Sc. degree in electrical engineering from Maua Institute of Technology (IMT), Brazil, in 1982, and the M.Sc. and Doctor degrees in electrical engineering from University of Sao Paulo (USP), in 1990 and 1999, respectively. His research interest includes microwave chemistry, passive microwave devices, antennas, RF/thermal analysis, and computational methods in electromagnetics. He has served as the President of the Brazilian Microwave and Optoelectronics Society (SBMO) in 2006-2008. Dr. Pouzada is a member of SBMO, AMPERE Europe, and the Institute of Electrical and Electronics Engineers, Inc. – IEEE.

Renata Borges do Nascimento received her B.Sc. degree in chemical engineering from Maua Institute Technology, and a M.Sc. degree in chemical and biochemical process engineering from the same institution. She is currently working toward the Doctor degree at the Federal University of ABC. She works as a General Chemistry instructor and researcher at Maua Institute Technology. She has experience in chemical engineering with emphasis on the development of chemical processes, working mainly on the following themes: development of chemical processes, application of microwaves in chemical processes, and chemical reactions enhanced by microwaves.

Edmilson Renato de Castro received the M.Sc. and Doctor degrees in metallurgical engineering from University of Sao Paulo in 2009 and 2016, respectively. He received the B.Sc. in chemical engineering from the Oswaldo Cruz School of Chemistry in 2000. He is currently an instructor and researcher at the Maua Institute of Technology, Brazil. He has experience in chemical engineering and microwave engineering, with emphasis on the development of chemical processes, application of microwaves in chemical processes, chemical reactions assisted by microwaves, working mainly in the following topics: carbothermic processes of metal oxides with microwaves. He is author and co-author of several scientific publications and patents.

JOSÉ THOMAZ SENISE received his B.S. in Mechanical and Electrical Engineering from University of Sao Paulo (1947), M.Sc. in Electrical Engineering from Stanford University (1955) and Ph.D. in Electrical Engineering from Stanford University (1959). His experience in Electrical Engineering is centered on microwave scientific and industrial applications, microwave chemistry, and biological effects of non-ionizing radiation. Dr. Senise is Honorary President of the Brazilian Microwave and Optoelectronics Society (SBMO), Professor Emeritus of Maua Institute of Technology (IMT), Researcher Emeritus of the Brazilian National Council for Scientific and Technological Development (CNPq).

Bárbara Betin Mente received the B.Sc. degree in chemical engineering from Maua Institute of Technology (IMT). She developed undergraduate research at the Microwave Laboratory of IMT. She was involved in a group study on Green ethylene production with microwaves, which was the winner of the Chemical Regional Council Award in the Chemical Engineering category, and also received the Odebrecht Company Award for Sustainable Development in 2015.

Mônica Caroline Martins received the Bachelor degree in chemical engineering from Maua Institute of Technology (IMT). She was a former trainee at Rhodia Solvay Group in the Operational Excellence area; she currently works as a Chemical Engineer at Foseco Vesuvius Corporation on the Process & Production Engineering area, Binders & Coatings sector. She currently works towards a MBA degree in Logistics and Production. She was involved in a group study on Green ethylene production with microwaves, which won the Chemical Regional Council Award in the Chemical Engineering category, and also received the Odebrecht Company Award for Sustainable Development in 2015.

Suzana Mayumi Yamaguchi received the B.Sc. degree in chemical engineering from Maua Institute of Technology (IMT), and was a former trainee at Promon Engineering Company, Brazil. She was involved in a group study on Green ethylene production with microwaves, which was the winner of the Chemical Regional Council Award on Chemical Engineering category, and also received the Odebrecht Company Award for Sustainable Development in 2015.

Viviane Ciola Sanchez received the B.Sc. degree in chemical engineering from Maua Institute of Technology (IMT). She developed undergraduate research at the Microwave Laboratory of IMT, and was a former trainee at Raizen Combustíveis, Brazil. She was enrolled in the Brazilian governmental program “Ciencias sem Fronteiras” studying at Technische Universität Gergakademie Freiberg, Germany. She was involved in a group study on Green ethylene production with microwaves, which won the Chemical Regional Council Award in the Chemical Engineering category, and also received the Odebrecht Company Award for Sustainable Development in 2015.