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New process to obtain unslaked lime through microwave hybrid heating and its fluid dynamics computational modeling

Novo processo de calcinação por aquecimento híbrido em microondas e modelagem através da fluidodinâmica computacional

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Breno Henrique Booz Carvalho Corrêa
ORCID: https://orcid.org/0000-0002-6934-9687
UFSJ-Brazil
E-mail: brenobooz@hotmail.com
Juan Canellas Bosch Neto
ORCID: https://orcid.org/0000-0002-2719-7689
E-mail: jboschbr@ufsj.edu.br
UFSJ-Brazil
Alexandre Bôscaro França
ORCID: http://orcid.org/0000-0001-5351-8581
UFSJ-Brazil
E-mail: alexandre.boscaro@ufsj.edu.br
Ana Clara Cassin Cordeiro
ORCID: https://orcid.org/0000-0001-5977-8544
UFSJ-Brazil
E-mail: anacassin26@gmail.com

Resumo

Os tratamentos térmicos de materiais através do uso de microondas vêm sendo utilizados na pesquisa e no desenvolvimento de diversos tipos de materiais como, por exemplo, nos materiais cerâmicos. Nesse tipo de processamento, a energia é transferida diretamente no interior do material através de processos de interação molecular e atômica com o campo eletromagnético. Os objetivos do presente trabalho foram desenvolver um novo processo de calcinação do calcário utilizando o aquecimento híbrido promovido pela junção das microondas e de um refratário cerâmico revestido internamente por óxido de cobre. Os objetivos específicos do trabalho foram o cálculo do custo energético do processo, a comparação do custo energético com processo convencional de calcinação, modelagem cinética do processo e a modelagem da calcinação por fluidodinâmica computacional. Analisou-se o comportamento de calcinação das rochas de calcário com diferentes massas e variações no tempo de retenção, utilizando a mufla e o microondas com e sem o uso de refratário cerâmico, com posterior análise da cinética química de decomposição do calcário e modelagem por fluidodinâmica computacional do processo em regime transiente. Como resultado da calcinação no microondas com o susceptor mostrou-se um processo que leva aproximadamente duas vezes mais rápido do que os métodos convencionais. Além disso, houve redução de 66,1% no gasto de energia. Observou-se também que o novo procedimento oferece vantagens na redução da emissão de gases de efeito estufa por liberação de apenas uma substância, facilidade no tratamento do ar em ambientes industriais e por ser um processo mais viável economicamente para a calcinação do calcário, que pode ser posteriormente aproveitado por empresas pertencentes a esse setor.

Palavras chave: Calcinação. Micro-ondas. Aquecimento híbrido.

Abstract

The thermal treatments of materials through the use of microwaves have been used in the research and development of several types of materials, such as, for example, ceramic materials. In this type of processing, energy is transferred directly into the material through processes of molecular and atomic interaction with the electromagnetic field. The objectives of the present work were to develop a new limestone calcination process using hybrid heating promoted by the combination of microwaves and a ceramic refractory coated internally with copper oxide. The specific objectives of the work were the calculation of the energy cost of the process, the comparison of the energy cost with a conventional calcination process, kinetic modeling of the process and the modeling of calcination by computational fluid dynamics. The calcination behavior of limestone rocks with different masses and variations in retention time was analyzed using muffle and microwave with and without the use of ceramic refractory, with subsequent analysis of the chemical kinetics of limestone decomposition and modeling by fluid dynamics computational analysis of the process in transient regime. As a result of microwave calcination with the susceptor, a process has been shown to take approximately twice as faster as conventional methods. In addition, there was a 66.1% reduction in energy expenditure. It was also observed that the new procedure offers advantages in reducing the emission of greenhouse gases by releasing only one substance, easing the treatment of air in industrial environments and because it is a more economically viable process for calcining limestone, which can later to be used by companies belonging to this sector.

Keywords: Unslaked lime. Microwave. Hybrid heating.

1. Introduction

In the context of world economy, quicklime is among the ten most widely used mineral products. Due to its versatility, it is present in various activities and has a significant importance in chemical, petrochemical, food, fertilizer and construction industries, among others. As it is a product that has been widely used in various sectors of the economy, its consumption is directly due to countries development. Recently, under the influence of chemical engineering research, lime manufacture is rather promising in industrial terms due to having a more refined process of technical control and being a material with greater uniformity that can be produced at a lower cost, (Chen, 2017).

Calcination is the main unit operation performed by lime industries which has some peculiarities and requires specific knowledge in order to produce good quality lime. Thereby it is important to analyze factors such as calcination temperature, particle size, impurities and reaction time. Calcination is an endothermic reaction which uses coal combustion in a rotary kiln to achieve desired temperatures in conventional processes. However, this heating process is environmentally unfriendly and consumes an excessive amount of energy. Thus, microwave hybrid heating has been proposed to increase limestone temperature to desired levels. It is a phenomenon used in modern industrial applications whose advantages are numerous, such as: time and energy savings, extremely fast heating rates, enhanced mechanical properties and considerably reduced processing time, (Hartlieb, 2016).

Thereby, the advance of alternative heating technologies has been the touchstone of this project so as to assess the possibility of energy reduction in microwave limestone calcination by increasing reaction speed and, consequently, achieving a decrease in calcination time and manufacturing costs.

Lime production is a consequence of limestone decomposition under heating conditions in industrial rotary kilns. Quicklime is a white inorganic material whose crystal structure is composed of single crystals or crystalline clusters of various sizes and intercrystalline gaps only observable by microscopy (Hwang *et al.*, 2015). A calcination reaction is described in Equation (1).

$$CaCO_3 + 3180\,kJ \rightarrow CaO + CO_2 \qquad (1)$$

The basic parameters affecting calcination processes is heat supply (temperature) and the stage of gas generation (pressure). In order to achieve limestone decomposition, temperatures ranging between 900 and 1100 °C should be reached so that calcination can occur not only on the surface of limestone, but towards the material's core (Rianna *et al.*, 2019). By heating limestone rocks to 882 °C, there is initially an increase in its volume. Once their surfaces are calcined, pore volume increases which allows releasing carbon dioxide (Navarro and Burgos, 2017). The input temperature of the reaction is 882 °C. As the reaction progresses towards the rock's core, the layer of CaO increases resistance to heat transfer, thus requiring higher temperatures upon the surface of rocks. For smaller particles, the chemical reaction is the controlling step, while heat and mass transfer control the reaction input in the case of larger particles. The present calcination process kinetics follows the pattern described in Figure 1.

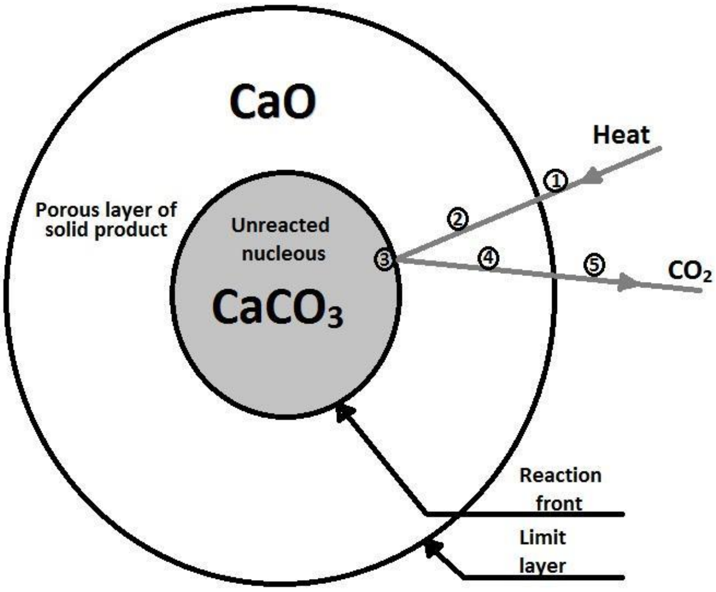

Figure 1 – Pattern of limestone chemical decomposition.

1. Heat transfer from the middle towards the surface of particles (typically convection).
2. Heat transfer through the layer that has already been decomposed for the reaction zone.
3. Chemical reaction in the reaction zone (utilizing the amount of heat introduced, CO_2 release, CaO slaking and recrystallization).
4. CO_2 diffusion through the CaO layer on the surface of particles.
5. CO_2 released from the particle surface into the environment.

The calcination process starts in warmer parts of limestone (in contact with the gas), i.e. from outside towards the inside, which evolve in the form of thermal waves towards its cold zones (inside the blocks). As it is the first layer to be formed in the calcination process, and there is considerably less thermal conductivity than the rock does, lime causes that the calcined layer decreases its speed as it moves towards the block's core subjected to heat. Thus, according to the amount of particle size distribution in the muffle furnace and as heat is transferred throughout the heating and calcination zones, an undecomposed central zone (core) is often found in the calcined material, i.e. in the form of carbonate. Figure 2 shows a photograph of lime rocks produced in the Chemical Engineering Laboratory of UFSJ, *campus* Alto Paraopeba, with a core of non-calcined calcium carbonate.

Figure 2 – Lime rock with undissociated core carbonate.

This research aims to utilize microwaves for limestone calcination and to demonstrate their potential for energy in comparison with conventional calcination processes, with a subsequent analysis of the modeling process through the COMSOL Multiphysics® software.

2. Methods

To compare limestone calcination in a muffle furnace with microwave calcination, the experiment was analyzed in three parts: rocks calcined in a muffle furnace at 950 °C; rocks calcined in a microwave both with aid of a refractory ceramic internally coated with copper oxide; the fluid dynamics modeling by COMSOL Multiphysics® using heat transfer transient with at constant heat flux of 10000 W/m² to analyze the temperature reached by copper oxide at varying process times.

Thus, tests are performed with two types of mass and geometry of calcite. In part 1, it was selected four rocks weighing around 20 g (15 mm) and four around 80 g (60 mm). The residence time was 60 minutes and 210 minutes for the 20 g and 80 g of rock, respectively. The conventional muffle furnace had nominal voltage of 220 V, 10 A of current and power consumption in the order of 2.2 kW.

Next, the hybrid calcination technique was used with the refractory ceramic internally coated with copper oxide. Copper Cuo was chosen Copper oxide was chosen as a susceptor because it results in temperature ranges suitable for the calcination process. Other susceptors such as Si could also be used (Marinel *et al.*, 2019). The upper part of the refractory ceramic has 120 mm of outer diameter, 80 mm of inner diameter and is 40 mm deep where there is the copper oxide coat which is about 1.5 mm thick. A hole with 10 mm in diameter was made in the core for microwave input to occur directly on the susceptor surface, thereby ensuring greater interaction with copper oxide using microwave energy. The lower portion is also 120 mm in diameter and 25 mm wide, whose base diameter is approximately 7 mm and 3 mm thick. Figure 3 illustrates refractory ceramic.

Figure 3 – Refractory ceramic cylinder internally coated with copper oxide.

In this part 2, it was selected eight rocks varying their masses and geometries likewise. Residence times ranged from 30 minutes to 150 minutes, thus achieving high efficiency. Their brand is Electrolux, model MEF28 with 18 L of capacity, rated voltage of 127 V, current of approximately 10.1 ampere, power consumption of 1,140 kW and microwave frequency of 2.450 GHz.

Before calcination trials were performed, a refractory shield was used called as kaolin clay, i.e. a compound of various hydrated silicates, in order to prevent physical damage to the muffle furnace due to high temperatures reached by copper oxide. One of which was made by adding 50% of oil to this substance and 50% of water in a 250 ml beaker and the refractory parts that would come into contact were coated.

In order to check the effect of residence time and mass reduction of calcite within the muffle furnace or microwave oven, a study was conducted to compare the actual reason for calcination with the ideal reason for calcination. The ratio of actual calcination was calculated using Equation 2.

$$Calcination\ ratio = \frac{mass\ after\ calcination}{mass\ before\ calcination} \tag{2}$$

As aforementioned, calcination occurs according to Equation 1. The reaction whose stoichiometry is 1:1 in which 100.0869 g/mol of $CaCO_3$ can produce 56.0774 g/mol of CaO (quicklime) releases 44.0100 g/mol of CO_2 into the atmosphere. Thus, in order to achieve 100% of calcination efficiency, optimal annealing ratio must be 0.5603, that was reached, approximately, for all rocks. For part 3, modeling was performed and discussed in the next topic.

2.1. Kinetic Model

According to literature, decomposition kinetics of limestone generates a sigmoidal curve. Decomposition is slow in its early stages, but afterwards there is rapid decomposition and lastly deceleration. At the beginning of the reaction, there is an induction period, then the reaction core is formed followed by an autocatalytic process. At the end of the process, deceleration results from solid reagent exhaustion. A model for decomposing limestone has been proposed by Prout and Thompkins according to Equation 3. Where x is conversion, t is time and C is a constant.

$$ln\, ln\, \left[\frac{x}{1-x}\right] = k * t + C \tag{3}$$

2.2. Computational fluid dynamics for microwave experiment

The Equations used for Computational Fluid Dynamics were the Continuity, Momentum and Energy Conservation, according to Equations 4, 5, 6. The ceramic support was geometrically designed through external software run in order to perform CFD analysis and the system contour conditions were given. Thereby, a mesh has been generated and the processing the result was obtained. Table I shows physical parameters to the simulation Computational Fluid Dynamics.

Continuity equation

$$\frac{\partial u_i}{\partial x_i} = 0 \tag{4}$$

Momentum conservation

$$\frac{\partial u_x}{\partial t} + \frac{\partial \left(u_i u_{xj}\right)}{\partial u_j} = -\frac{1}{\rho}\frac{\partial p}{\partial x_i} + v\frac{\partial .2u_i}{\partial x_j^2} + g_i \tag{5}$$

Energy conservation equation

$$\rho\, C_p \frac{\partial T}{\partial t} + \rho\, C_p \nabla .(uT) = k.\nabla^2 T + \Phi_v \tag{6}$$

Maxwell’s Equation Electromagnetic waves

$$\nabla\, x\, \left(\frac{1}{\mu'}\ \nabla\, x\, E^{=}\right) - \left(\frac{\omega^2}{c^2}\right)\left(\epsilon' - j\epsilon''\right) E^{=} = 0 \tag{7}$$

The modelling of microwave heating is governed by Maxwell’s Equation (7). Electromagnetic waves, frequency domain. A rectangular port with transverse electric mode is employed in this physics model to represent the microwave generator (magnetron). Where μ' is the relative permeability, $\bar{E}$ is the electric field intensity inside the microwave cavity (V/m), ω is the angular frequency (rad/s), c is the speed of light in free space (3×108 m/s), ϵ' is the relative permittivity or dielectric constant, and ϵ'' is the relative dielectric loss of a material. Dielectric constant measures the ability of a material to store electrical energy whereas dielectric loss indicates the ability of a material to loss the electrical energy as heat energy.

The model simulates a limestone one cube calcined using a microwave heating technique. The Table I shows physical parameters to the CFD simulation.

Table I – Physical parameters to the CFD simulation

Materials	Thermal conductivity/ $W.m^{-1}.K^{-1}$	Density/ $kg.m^{-3}$	Heat capacity/ $J.kg^{-1}\cdot K^{-1}$	Relative permeability	Dielectric constant
Cooper oxide (CuO)	17.99	6500	536	104	10000
Ceramic fiber	0.325	2730	1130	1.10	21,8
Limestone	2.5	1920	0.90	1,00	10,0

3. Results

The results were plotted on two charts, yielding Figures 4 and 5. Figure 4 shows thermal decomposition using a microwave oven and muffle furnace for two calcareous mass: 20 grams and 80 grams. It is observed that the process using the microwave with the ceramic capsule coated with copper oxide is approximately twice as fast than that in the muffle furnace.

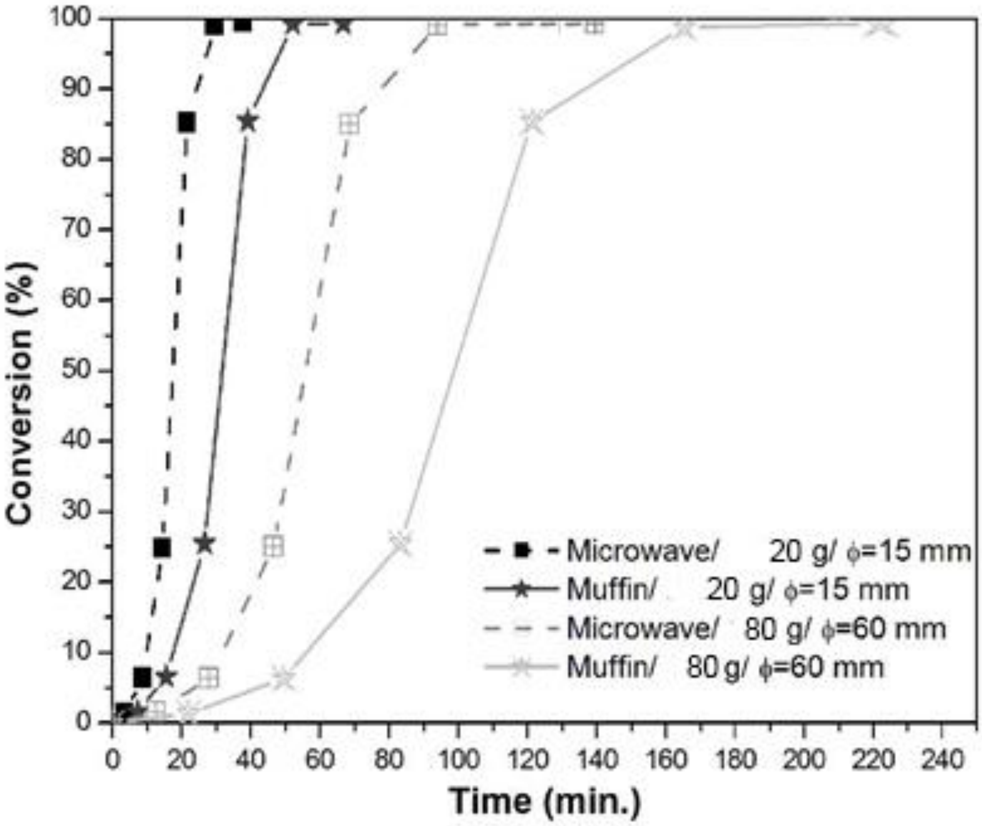

Figure 4 – Chart of Calcination Ratio as a function of retention time for the muffle furnace

Figure 5 shows the fit according to Prout and Thompkins model with the determination of parameters k. It is observed that k rate constants for microwaves are significantly higher than the rate constants for the muffle furnace. The kinetic constant for the 15 mm calcareous diameter was 25 times higher in the microwave than in the muffle furnace. The kinetic constant for the 60 mm calcareous diameter was twice as much in the microwave as in the muffle furnace. The larger the calcareous exposed area is, the greater the calcination process efficiency becomes.

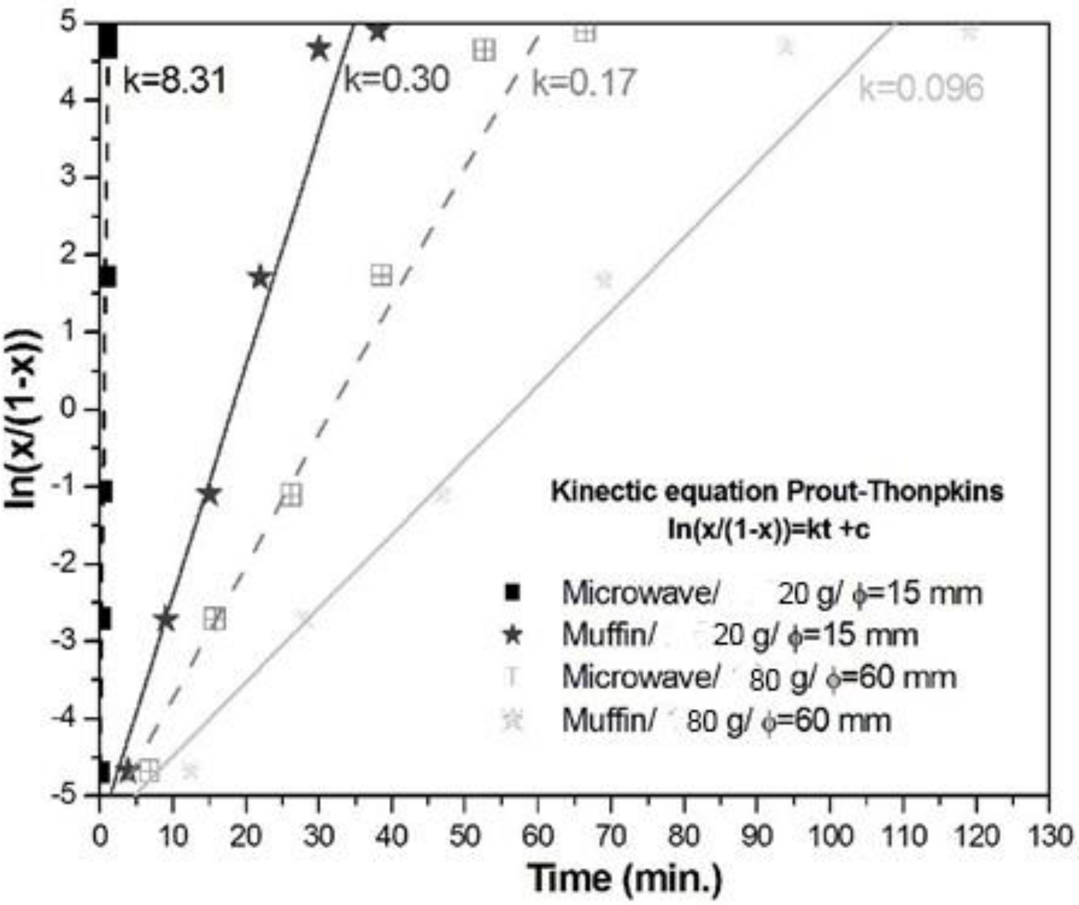

Figure 5 – Calcination kinetics of microwave and muffle furnace

The results obtained for the muffle furnace are similar to those obtained by Kale (2002). It was observed that the benefits of using the aforementioned microwave are only obtained when calcination is performed with control and scientific understanding of the set of parameters and aspects involved. Initially, it was aimed to calcine limestone rocks by direct microwave heating, but it was found a significant number of key issues.

Many rocks feature small energy absorption of microwaves at low temperatures, due to small molecule movement toward the generated electromagnetic field, thus hindering initial heating. It was noted that even by promoting rock comminution, surface area increased, thus being a great reaction.

Another problem is that thermal instabilities can occur during heating which leads to the phenomenon of thermal runaway, thus resulting in an exponential increase in temperature and catastrophic heating of the sample. A variety of materials behave similarly, including ceramics such as Al2O3, SiO2, Fe3O4, β-alumina and ZrO2 (Menezes, Souto and Kiminami, 2007). Finally, the characteristic temperature gradient present during volumetric heating may lead to severe temperature variations of calcite. Then, inserting the hybrid heating with the ceramic refractory coated with copper oxide, we obtained an optimum range of the real calcination ratio, with reaction efficiency around 98.82 % twice as fast as the conventional method. Figure 6 depicts the rock before and after hybrid heating in the microwave.

Figure 6 – 20 g rocks before and after calcination in the microwave.

In Figure 7, it can be observed a fluid dynamics computational modeling of temperature profile inside the oven for 50 minutes of heating time at temperatures of around 1160°C. Modeling results were similar that observed in the experiments. The simulation was set to all thermodynamic properties according to the type of material used in the experiments, in which thirty-two temperature measurements of the transient process.

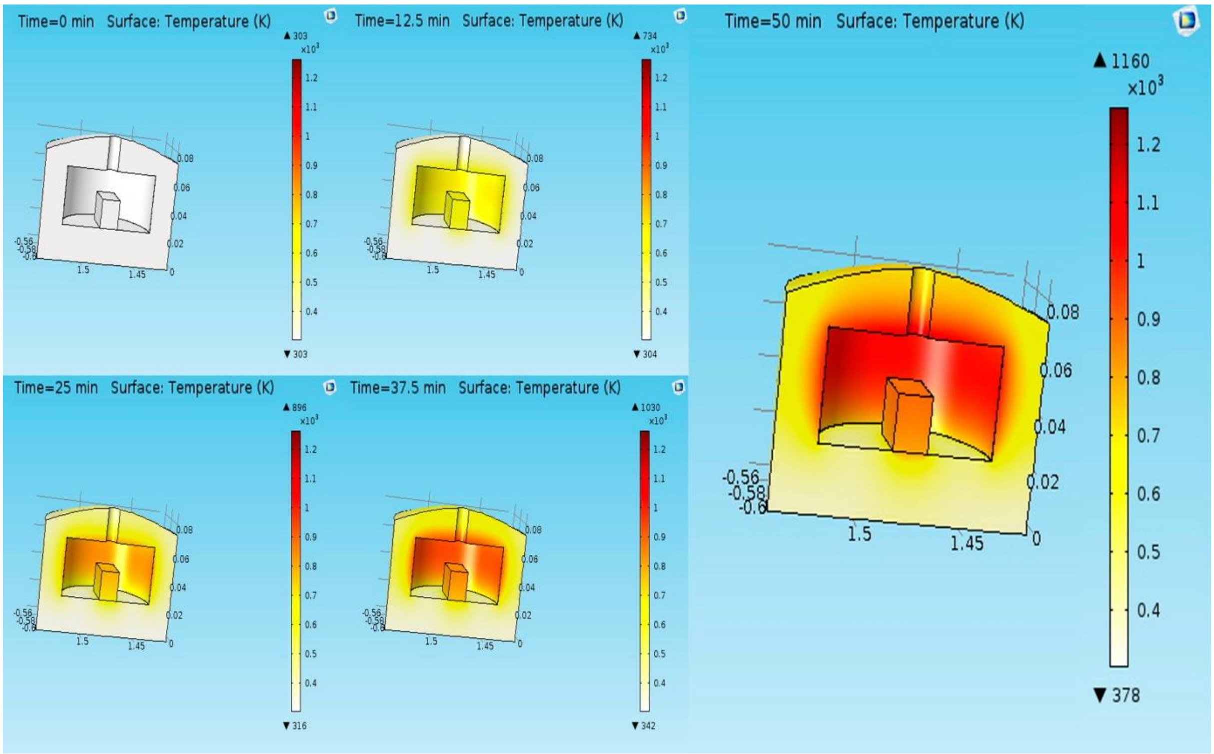

Figure 7. Temperature gradient in COMSOL Multiphysics®.

Table 2 below shows the power consumption by the muffle furnace and microwave oven according to each test performed.

Table 2. Calculation of energy consumed by each equipment.

Energy consumed by the muffle furnace			Energy consumed by the microwave		
Power /kW	**Time /min**	**Energy/ kWh**	**Power/ kW**	**Time /min**	**Energy/ kWh**
2.20	120	4.40	1.14	50	0.95
2.20	170	6.23	1.14	66	1.25
2.20	180	6.60	1.14	83	1.58
2.20	230	8.43	1.14	100	1.90
-	-	-	1.14	116	2.20
-	-	-	1.14	133	2.53
-	-	-	1.14	150	2.85

It can be observed that the energy consumed by the microwave during a longer calcination period, was only 2.85 kWh, about 2.96 times lower than the energy used to calcine the rocks in the oven in its longest period, i.e. 8.43 kWh. A reduction of 66.1% in energy expenditure was obtained. This result reveals that the process is economically and environmentally feasible. It is worth mentioning that the fuel used for the rotary kiln operation in industries has great influence on product quality and manufacturing costs. Fuel costs currently amount to 60% of total production costs. Furthermore, 70% of the costs of fuel consumption are associated with the rotary kiln operation (Soares, 2007).

The least amount of energy required for the thermal decomposition process of limestone at temperatures close to 1173 K (900 ° C) is about 3029 kJ (723Kcal) which is produced per kg of CaO. Since the heat energy of the decomposition reaction in standard conditions of 298 K (25 °C) is 3184 kJ/kg (760 kcal/kg) of CaO, the total heat of modern rotary kilns is around 3600 kJ/kg (860 kcal/kg) of CaO (Soares, 2007).

Due to the fact that limestone calcination processes have traditionally been carried out by burning fossil and non-renewable fuels, such as oil, coal, or natural gas, a lime production plant releases CO2 as byproduct of both the calcination reaction and the combustion process that provides the reaction with energy. Lime industries produce 5% of all synthetic CO2 available, 40% is from chemical processes and 60% from burning fossil fuel.

These features allow heating large parts quickly and uniformly, without generating high thermal stresses that can cause cracks or damage parts. As microwave energy absorption varies according to the composition and structure of phases, selective heating is also possible.

In several experiments and studies on microwave in sintering, thermal insulation systems have been used to minimize these gradients and achieve optimum temperature reaction conditions (Menezes, Souto and Kiminami, 2007). However, the use of insulation systems can seriously exacerbate the problem of thermal runaway which has led to the development of hybrid heating techniques that combine heating with microwaves and infrared heat sources. The application of microwave energy to rapid sintering leads to a significant intensification of the processing difficulties mentioned above. However, the benefits of rapid sintering have influenced several studies on ways to overcome these obstacles.

Hybrid heating can be accomplished either with the aid of a conventional heating system such as resistance or gas burners, or with by using materials with high dielectric loss at low temperatures, otherwise known as susceptors. These materials absorb microwave energy by turning them into thermal energy, or heating the sample with a similar electrical resistance used in conventional heating. It also enables rapid heating of materials through microwave at low temperatures and thermal gradients soften at high temperatures, which are commonly used to produce ceramic with high and low dielectric loss (Menezes, Souto and Kiminami, 2007).

Through this knowledge found in literature, few adjustments were made and the process has been repeated with hybrid microwave ashing using copper oxide as susceptor, thus becoming an innovative process. The susceptor was chosen based on a study conducted by Michail Samouhos, Ron Hutcheon and Ioannis Paspaliaris (2011). Comparisons were made between susceptors CuO and malachite by a differential thermal analysis (DTA). The experiment was conducted using a TG-C-DS Labys system at temperatures ranging between 25-1300 °C and CuO for the malachite concentrate between 25-1100 °C at a heating rate of 10 °C/min and air atmosphere.

The process describe in this work was patented and accepted on May 26, 2020 at the Instituto Nacional da Propriedade Industrial (INPI), under registration number BR2020180730024.

4. Conclusion

Lime has great economic importance on account of having various applications, such as the chemical treatment of water. This paper has presented an analysis of the calcination process of limestone to obtain lime by comparing the energy, economic and environmental efficiency of use a microwave oven in the process.

The calcination process using the microwave oven through which it was observed that limestone calcination through a microwave provides the best results in terms of reaction time, energy consumption and emission of polluting gases. Microwave calcination with a refractory ceramic coated with copper oxide guaranteed a process to be approximately twice as fast as conventional methods, in addition, a reduction of 66.1% in energy expenditure was obtained. It was also found that the new procedure offers advantages regarding the reduction of greenhouse gas emissions, that is, only one substance is released, facilitating the treatment of air in the industrial environments in question.

It is concluded that it is interesting to calcine calcareous having smaller diameters in the microwave (15 mm) in order to achieve a calcination process with greater efficiency, since the kinetic constant for the 15 mm calcareous diameter was 25 times higher in the microwave than in the muffle furnace. A larger calcareous exposed area reveals great efficiency of the calcination process.

Modeling results were similar that observed in the experiments. The simulation was set to all thermodynamic properties according to the type of material used in the experiments, in which thirty-two temperature measurements of the transient process.

Quicklime obtained through the hybrid microwave heating achieved the initial objectives, due to being more economical and viable in the limestone calcination process (calcite), thus it may be further used by industries belonging to this sector. Therefore, as further research, it is recommended to develop a prototype on a pilot scale which is able to achieve a higher volume of lime production, thus bearing closer resemblance to the reality of Brazilian industries.

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