Comparative Evaluation of Acid and Basic Thermo-Chemical Treatments in the Production of Adsorbents Based on Biodiesel Production Solid Residue

Tatiana M. Barbosa, Adriana S. Franca, Leandro S. Oliveira, and Ramon M. Valle

***Abstract*—Raphanus sativus press cake, a solid residue from biodiesel production, was evaluated as precursor material for the production of adsorbents. A comparative evaluation of acid and basic activating agents is presented, as well as conventional and microwave carbonization. The treatment that provided best adsorption performance was microwave activation employing KOH. Characterization results pointed to a homogeneous and porous adsorbent surface, and results from both kinetics and equilibrium essays indicated that methylene blue adsorption was probably taking place at the surface. Adsorption kinetics and equilibrium were satisfactorily described by the pseudo second-order and Langmuir models, respectively. Adsorption tests showed that the prepared adsorbents presented higher adsorption capacity than activated carbons produced from other agricultural residues, confirming that this type of waste material is a suitable candidate for use in the production of adsorbents.**

***Index Terms*—Adsorption, biodiesel residue, dye removal.**

I. INTRODUCTION

Wastewaters containing dyes are generated by several industries such as textile, leather, paper, cosmetics, food and others. Such wastewaters contain dyes, hazardous materials that have severe negative environmental impacts when discharged without adequate treatment [1]. Because of the high toxicity of dyes and their employment in a wide variety of industries, there have been many studies aiming at dye removal from wastewaters [2].

Adsorption using activated carbons (AC) has been extensively employed for decolorization of aqueous solutions, because it is usually more effective and less expensive than the other commonly employed physical and chemical processes [3]. However, it still has some disadvantages including high cost of the AC and the need for its regeneration, among others. Such disadvantages have prompted a growing research interest in AC production from renewable and low-cost materials, mostly agricultural by-products (lignocellulosic materials), and comprehensive reviews on this subject are available in the literature [2]-[4].

Recent studies have demonstrated the potential of non-edible oils for biodiesel production, employing *Raphanus sativus L.* seeds (RS) oil [1], [5]. However, this process generates a significant amount of solid residues, e.g., pressed seed cakes. These solid residues present environmental problems in terms of adequate disposal, given their limited applications as animal feed, silage or energy source, thus reinforcing the need for alternative uses. A few recent studies have shown that this type of residue (oilseed press-cakes from biodiesel production) can be used for AC production [1], [6]-[8].

The transformation of lignocellulosic or other carbon based material into ACs can be classified as 1) physical or 2) chemical activation. Physical activation consists on thermal treatment of the material, being usually carried out in a two-step process: 1) carbonization in the presence of an inert gas (usually N_2) to produce the charcoal, followed by 2) a second heat treatment (activation) in the presence of CO_2 or steam. The goal is to increase the porosity of the material. Chemical activation is performed by impregnating the carbon-based material with an activating agent followed by heat treatment. In this case, both the carbonization and activation steps are carried out in a single step. This process is usually considered to be more advantageous in comparison to physical activation, because it can be carried out at lower temperatures (lower energy costs and higher yields) and produces both micro and mesoporous adsorbents [9].

Microwaves have been extensively employed as an alternative heating method and several studies have demonstrated that this technique can be successfully employed in the production of ACs [1], [10]. Advantages of this technique over conventional heating for the production of ACs include reduction in processing time; reduction in energy consumption; reduction or sometimes elimination of the amount of gases employed; and, in the case of dye removal, improvement of adsorbent capacity [10].

In view of the aforementioned, and taking into account that the studies available in the literature on the use of RS press-cakes for production of adsorbents did not involve chemical activation [1], [8], the objective of this study was to compare thermo-chemical treatments in the production of adsorbents for dye removal. Both acid and basic activated agents were employed, as well as conventional and microwave carbonization.

II. METHODOLOGY

A. Adsorbent Preparation

The *Raphanus sativus* press-cake was washed and ground,

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The authors are with DEMEC, Universidade Federal de Minas Gerais, Av. Antônio Carlos 6627, Belo Horizonte, MG, 31270-901, Brazil (e-mail: mbtatiana@gmail.com, adriana@demec.ufmg.br, leandro@demec.ufmg.br, ramon@demec.ufmg.br).

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followed by contact with hot water (50°C) to remove excess oil. It was then dried (110°C, 24 h) and sieved (0.15 mm < particle diameter < 0.43 mm). This material was evaluated as a biosorbent (A1). This material was also submitted to carbonization (370°C, 2 h) in N_2 atmosphere and the produced charcoal was also evaluated as an adsorbent (A2). The muffle oven-based activation procedures consisted of treatment with the activating agent followed by 2 h carbonization in a muffle oven at 370 °C (acid activation with H_3PO_4 – A3; basic activation with KOH – A5 or NAOH – A7). The microwave-based activation procedures consisted on carbonization in a microwave oven (900 W, 5 cycles of 2 min; after each cycle the sample was stirred by hand with the aid of a glass rod), followed by mixture with the activating agent and drying (60°C, 24 h) (acid activation with H_3PO_4 – A4; basic activation with KOH – A6 or NAOH – A8). Afterwards, all the produced adsorbents were washed until pH 7 and dried again (60°C, 24 h). The adsorbent yield, defined as the weight of dried adsorbent (W_1) to the weight of dry raw material (W_o), was calculated as follows:

$$yield(\%) = \frac{W_1}{W_o} \times 100 \quad (1)$$

B. Adsorption Tests

Batch experiments of adsorption were performed in 250 mL Erlenmeyer flasks, with the flasks being agitated on an orbital shaker at 110 rpm. In all sets of experiments, the adsorbent was thoroughly mixed with 150 mL Methylene Blue (MB) at concentrations of 100, 300 and 500 mg L^{-1} and at a fixed adsorbent concentration (10 g L^{-1}). All tests were performed in two replicates. 2 mL aliquots were taken from the Erlenmeyer flasks at pre-specified time intervals and MB concentration was determined by UV–Vis spectrophotometer (Hitachi U-2010) at 665 nm. The amount of MB adsorbed, q (mg/g) was calculated by:

$$q = \frac{(C_o - C)V}{W} \quad (2)$$

where C_o and C (mg.L^{-1}) are the liquid-phase MB concentrations at initial and sampling times, respectively; V is the volume of the solution and W is the mass of dry adsorbent used.

C. Adsorbent Characterization

The surface morphology of selected adsorbents was examined using a scanning electron microscope (JEOL JSM-5510). The surface structure of the adsorbent that presented best performance in terms of MB removal was also investigated using Fourier Transform Infrared (FTIR) spectroscopy, before and after adsorption. The FTIR spectra were obtained and recorded on a FTIR spectrometer (IRAffinity-1, Shimadzu, Japan) operating in the range of 600–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Adsorbent Yield

The yields of the prepared activated carbons are presented in Table I and ranged from ~2-50%. Overall AC yields were lower for the ACs submitted to oven carbonization compared to the ones processed with microwaves, for a given activation agent. These differences in yield can be attributed to the fact that the conventional oven carbonization requires longer times and higher temperatures than microwave-induced methods, with consequent lower yields. Also, the activation agent had a significant effect on carbon yield, with higher yields observed for the acid activated carbons in comparison to the basic ones. A similar trend was reported in the literature for microwave-activated adsorbents based on other types of lignocellulosic residues [10]. However, the reported differences in yield were not as significant as the ones observed in this study, indicating the type of precursor material to be an important factor as well. Among the prepared adsorbents, A4 presented the highest yield, followed by A3 and A2.

TABLE I: ADSORBENT YIELD

Adsorbent (activation agent/carbonization)	Yield (%)
A2 (no activation/oven)	20.07
A3 (H_3PO_4/oven)	47.45
A4 (H_3PO_4/microwave)	51.08
A5 (KOH/oven)	17.00
A6 (KOH/microwave)	16.56
A7 (NaOH/oven)	1.60
A8 (NaOH/microwave)	18.25

B. Effect of Activating Agent

The results obtained for adsorption capacity varying with time for all the prepared adsorbents are shown in Fig. 1. These results show that both the activating agent and carbonization procedure have a significant effect on the adsorption capacity. The adsorbents with best performance were the ones that underwent basic activation (A6, A8) after microwave carbonization. Although A4 (acid activation in the microwave oven) resulted the adsorbent with the highest yield (Table I), it presented quite low adsorption capacity, similar to the charcoal without further activation (A2) and much lower than the original material without any thermal or chemical treatment (A1). Notice that microwave activation provided a significant increase in adsorption capacity in the case of the adsorbent prepared with KOH (A5 vs. A6). A similar behavior was reported in the literature, employing adsorbents based on both *Raphanus sativus* and other types of press cakes, but without any chemical activation [1], [6]-[8].

It should be pointed out that chemical activation promotes both chemical changes to the charcoal matrix and physical changes by favoring the creation of pores (by volatilization of organic matter). Also, because it alters the chemical makeup of the charcoal surface, the chemical agent invariably alters the final chemical functionality of the activated carbon surface and, hence, its affinity to specific adsorbates [9], [10]. In the case of basic activation, the carbon surface will obviously have a basic characteristic in association with the presence of carbonyl, chromene, pyrone and oxygen-free Lewis-type structures, whereas the acidic behavior is related to oxygen-containing groups (mainly carboxylic, anhydrides, lactonic and phenolic). In view of the previous results, the adsorbent prepared by microwave-based KOH activation (A6) was chosen for further evaluation.

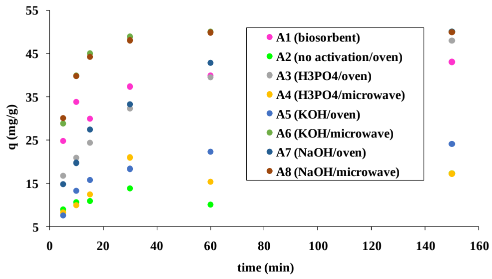
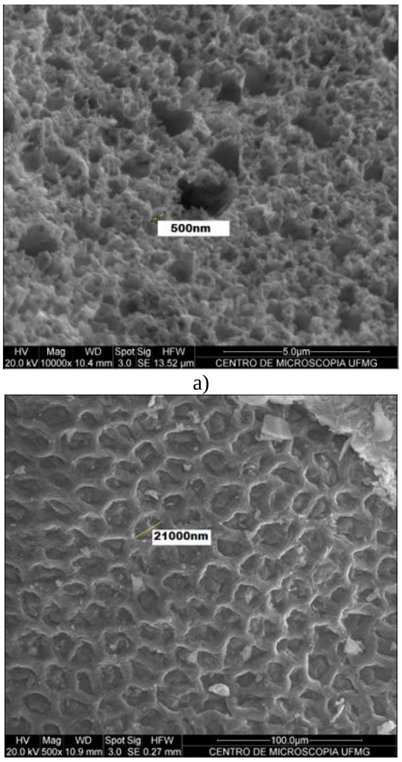


Fig. 1. Adsorption capacity of the prepared adsorbents (Initial MB concentration = 500 mg/L).

C. Adsorbent Characterization

SEM images of both the adsorbents prepared by KOH activation (A5, A6) are shown in Fig. 2. Surface porosity is evident in both adsorbents. Notice that the one prepared in the muffle oven (A5) presents a more heterogeneous surface. However, the one prepared in the microwave oven (A6) presents much larger pores, which is particularly interesting if the adsorbent will be employed for removal of large molecules such as dyes and pigments. This could explain was adsorption was faster and more effective for A6 in comparison to A5, and the corresponding higher value of adsorption capacity.



a)

b)

Fig. 2. Scanning electron micrograph (SEM) of the KOH activated adsorbents carbonized in a) muffle and b) microwave ovens.

The surface of the prepared adsorbent was further examined by FTIR spectroscopy and the corresponding spectra are displayed in Fig. 3. Although the differences between the spectra before and after adsorption are small, it can be noticed that there is a slight increase in bands in the region of 1700 to 400 cm^{-1} where the MB spectrum (also shown in Fig. 3) presents the highest peak intensity, corroborating its presence at the surface of the adsorbent. The lack of significant differences between the spectra before and after adsorption is suggestive of a π–π type of interaction to be the predominant adsorption mechanism.

D. Adsorption Kinetics

The batch adsorption data shown in Fig. 4 indicate that a contact time of 8 hours assured attainment of equilibrium conditions for initial MB concentrations of 100, 300 and 500 mg L^{-1}. Adsorption can be described as a two-stage process, with a rapid initial adsorption, followed afterwards by a slower rate. This type of behavior can be attributed to the high values of concentration gradient in the beginning of the adsorption processes, representing a significant driving force for MB transfer between the solution and the adsorbent surface. This qualitative behavior has been reported for MB removal by other types of adsorbents [6], [7]. Adsorption capacity increased with increased initial concentration as expected.

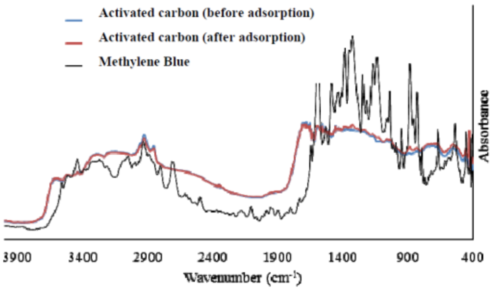


Fig. 3. FTIR spectra.

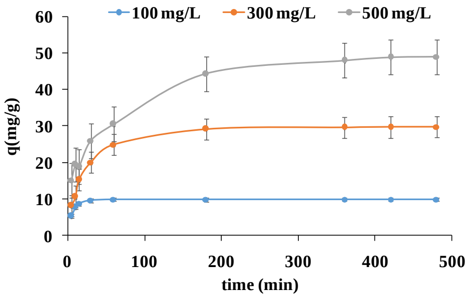


Fig. 4. Adsorption capacity vs. time for different values of initial MB concentration.

Adsorption kinetics was investigated by fitting pseudo first and second-order kinetic models to the experimental data [11]. The corresponding equations in integrated form are:

First-order kinetics (n=1):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{3}$$

Second-order kinetics (n=2):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

where q_e and q_t correspond to the amount adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium and at time t, respectively, and k_n corresponds to the rate constant for n^{th}

order adsorption.

Evaluation of each model's ability to predict the experimental data was based on both regression correlation coefficient values (r^2) and difference between experimental ($q_{t,exp}$) and model-estimated ($q_{t,est}$) values, evaluated by means of the error measure:

$$RMS = 100\sqrt{\sum \left[\left(q_{t,est} - q_{t,exp}\right)/q_{t,exp}\right]^2 / N} \qquad (5)$$

where N is the number of experimental points in each q_t vs. t curve.

Results for the non-linear fits of the kinetic models and their estimates for equilibrium adsorption capacity are shown in Table II. The pseudo-second order model provided higher r^2 values and lower values of RMS error in comparison to the pseudo-first order model, thus being selected as more adequate for description of the adsorption data, for all evaluated temperatures. This model has been successfully applied for description of adsorption kinetics of several adsorbates, in association with both chemisorption and ion exchange mechanisms [11]. It was also the more adequate model for description of MB removal in several types of adsorbents [6], [7], [12], [13].

The effect of diffusion as a possible rate-controlling step in the adsorption process was evaluated according to the intra-particle diffusion model [14]:

$$q_t = k_p t^{1/2} + C \qquad (6)$$

where k_p is the intra-particle diffusion rate constant, evaluated as the slope of the linear portion of the curve q_t vs. $t^{1/2}$. Results are displayed in Fig. 5 and the corresponding values of the constants are shown in Table II. The intra-particle diffusion plots can present up to four linear regions, representing boundary-layer diffusion, followed by intraparticle diffusion in macro, meso, and micro pores. These four regions should then be followed by a horizontal line representing the system at equilibrium [15]. The plots presented in Fig. 5 show one region followed by a plateau (100 mg/L) and two regions followed by a plateau (300 and 500 mg/L), indicating that boundary-layer diffusion seems to be the rate-controlling step. Also, the fact that none of the lines cross the origin are an indication that pore diffusion is not as important and that adsorption is probably taking place mostly at the external surface.

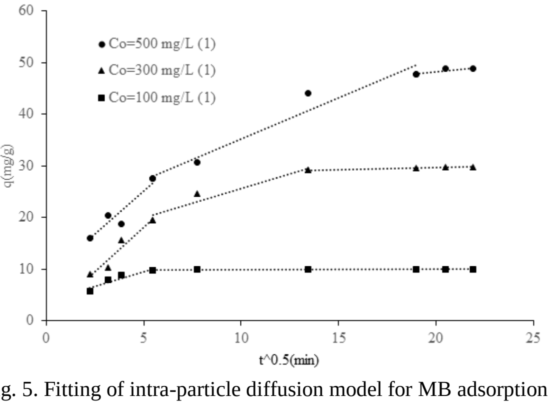


Fig. 5. Fitting of intra-particle diffusion model for MB adsorption.

TABLE II: KINETIC PARAMETERS FOR MB ADSORPTION

	MB initial concentration (mg L^{-1})		
	100	300	500
q_e (experimental)	9.918	29.740	48.826
Pseudo first-order			
k_1 (h^{-1})	0.006	0.012	0.012
q_e (estimated) (mg g^{-1})	9.856	28.990	46.001
r^2	0.993	0.959	0.839
RMS	0.510	4.492	8.187
Pseudo second-order			
k_2 (g $mg^{-1}h^{-1}$)	0.051	0.002	0.001
q_e (estimated) (mg g^{-1})	10.191	30.973	46.001
r^2	0.948	0.988	0.927
RMS	1.357	2.844	5.704
Intra-particle -diffusion			
ki (mg/g$h^{0.5}$)	0.119	0.967	1.683
C	7.785	11.462	15.442
r^2	0.433	0.811	0.945

E. Adsorption Equilibrium

The adsorption isotherm is shown in Fig. 6. The shape of the curve indicates favorable adsorption. In this study, we evaluated the following two-parameter models for equilibrium description: Langmuir, Temkin and Freundlich. Langmuir isotherm [16] is based on a theoretical model that assumes monolayer adsorption over an energetically and structurally homogeneous adsorbent surface, and can be represented by the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (7)$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) correspond to the amount adsorbed per gram of adsorbent and to the solute concentration (mg L^{-1}) in the aqueous solution, respectively, after equilibrium was reached. q_{max} and K_L are constants related to the maximum adsorption capacity (mg g^{-1}) and the adsorption energy (L mg^{-1}), respectively.

Temkin's model [17] is based on the assumption that the heat of adsorption of all the molecules in the layer decrease linearly with surface coverage due to adsorbent–adsorbate interactions. Therefore, adsorption is characterized by a uniform distribution of binding energies, up to a maximum value. This isotherm can be described by the following equation:

$$q_e = \frac{RT}{b} \ln\left(K_T C_e\right) \qquad (8)$$

where b is the Temkin constant related to the heat of sorption (J mol^{-1}), K_T is the Temkin isotherm constant (L g^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

Freundlich's equation, on the other hand, is an empirical model that does not account for adsorbent saturation and has been associated to both heterogeneous and multilayer adsorption. It can be described by the following equation:

$$q_e = K_F C_e^{1/n} \tag{9}$$

where K_F is a constant that indicates the relative adsorption capacity ($mg^{1-(1/n)}L^{1/n}\ g^{-1}$) and n is related to the intensity of adsorption [18].

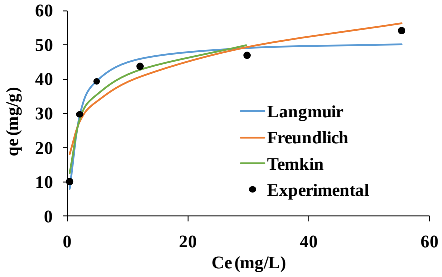


Fig. 6. Equilibrium isotherm (25°C).

TABLE III: Equilibrium Parameters for Phenol Adsorption

Model	Parameter values		R^2	RMS_e
Langmuir	$K_L = 0.69$	$q_{max} = 51.7$	0.975	3.844
Temkin	$K_T = 18.3$	$RT/b = 7.95$	0.973	4.649
Freundlich	$K_F = 24.8$	$1/n = 0.212$	0.899	13.879

TABLE IV: Comparison of Monolayer Maximum Adsorption Capacity of Several Residue-Based Adsorbents for MB Removal

Precursor	Treatment	q_{max} (mg/g)	Ref.
Pressed seed cakes			
Raphanus sativus	microwave/KOH	51.7	This study
Raphanus sativus	microwave	29.9	[1]
Defective coffee beans	oven	14.9	[6]
Defective coffee beans	microwave	68.5	[7]
Raphanus sativus	oven	18.3	[8]
Sunflower seeds	oven/ H_2SO_4	16.4	[13]
Other materials			
Date pits	oven/CO_2	12.9-17.3	[12]
Coconut husks	oven/ H_2SO_4	17.2	[19]
Coconut husks	oven/ KOH	435	[20]
Clay	H_2SO_4	25.0	[21]
	$Al(OH)_3$	62.5	
Hazelnut husks	oven/ $ZnCl_2$	8.8	[22]
Avocado seeds		4.1	
Walnut husks		3.5	
Sugarcane bagass	EDTA	202	[23]

Model selection was based on highest R^2 values coupled with the lowest difference between calculated and experimental q_e values, evaluated according to the following root mean square error measure:

$$RMS_e = 100\sqrt{\sum \left[\left(q_{e,est} - q_{e,exp}\right)/q_{e,exp}\right]^2 / N} \tag{10}$$

where $q_{e,exp}$ and $q_{e,est}$ are the experimental and model estimated equilibrium adsorbent amounts, respectively, and N corresponds to the number of experimental isotherm points. The calculated model parameters are displayed on Table III. An evaluation of both R^2 and RMS_e values show that MB adsorption was better described by the Langmuir and Temkin models, indicating homogeneous and monolayer adsorption, consistent with the assumption of a predominant π–π type of interaction between adsorbent and adsorbate. This model also provided the best description for MB removal by other microwave activated carbons [7].

A comparative evaluation of several residue-based adsorbents employed for MB removal is shown in Table IV. Notice that the adsorbent prepared in this study presented satisfactory capacity in comparison to other adsorbents, indicating that this precursor material can be used in the production of adsorbents for wastewater treatment. Results also show that both the precursor material and the type of treatment employed will have a significant impact on adsorbent capacity.

IV. Conclusion

Raphanus sativus press-cake was shown to be a feasible precursor material for the production of adsorbents. Several acid and basic activation methods, using either conventional or microwave carbonization were tested. The treatment that provided the adsorbent with best performance in terms of methylene blue removal was microwave activation employing KOH. Adsorption kinetics was better described by a pseudo second-order model, and results indicated that boundary-layer diffusion seems to be the rate-controlling step and that adsorption is taking place mostly at the external surface. Equilibrium was better described by the Langmuir and Temkin models, indicating homogeneous and monolayer adsorption. Our results confirm the potential of using biodiesel solid residues for wastewater treatment, given that the prepared adsorbent presented higher adsorption capacity in comparison to activated carbons produced from other agricultural residues. Future studies will be focused on evaluation of such adsorbent for removal of other types of polutants (organics, heavy metals) and also on fixed-bed tests aiming at industrial applications.

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Tatiana M. Barbosa was born in 1988 and graduated in chemical engineering from Centro Universitário de Belo Horizonte, Brazil, in 2012. She has just obtained her master's degree in mechanical engineering at UFMG. This paper represents part of her M.Sc. dissertation, developed under supervision of Prof. Adriana S. Franca.

Adriana S. Franca was born in 1966, graduated in chemical engineering in 1988 and obtained her M.Sc. degree in mechanical engineering in 1991 from Universidade Federal de Minas Gerais, Belo Horizonte, Brazil. She completed her Ph.D. in agricultural and biological engineering from Purdue University, USA, in 1995.

She is currently a professor at the Department of Mechanical Engineering from Universidade Federal de Minas Gerais and also teaches at the graduate course in food sciences. She has published 80 articles in international journals, 16 book chapters and has presented several research papers at various international conferences held in Brazil and abroad. Her research interests include sustainable uses of agricultural residues, coffee chemistry, microwaves, FTIR and others.

Leandro S. Oliveira was born in 1964. He graduated in chemical engineering in 1988 and obtained his M.Sc. degree in mechanical engineering in 1991 from Universidade Federal de Minas Gerais, Belo Horizonte, Brazil. He completed his Ph.D. in agricultural and biological engineering from Purdue University, USA, in 1995.

He is currently a professor at the Department of Mechanical Engineering from Universidade Federal de Minas Gerais and is currently the head of the graduate program at that Department. Dr. Oliveira also teaches at the graduate course in food sciences. He has published over 70 articles in international journals, 13 book chapters and has presented several research papers at various international conferences held in Brazil and abroad. His research interests include sustainable uses of agricultural residues, adsorption, biofuels, coffee chemistry, and others.

Ramon Molina Valle was born in 1953, graduated in chemical engineering in 1979 and obtained his M.Sc. degree in mechanical engineering in 1984 from Universidade Federal de Minas Gerais, Belo Horizonte, Brazil. He obtained his doctorate degree in mechanical engineering from Universidade Federal de Santa Catarina, Brazil, in 1995.

He is currently a professor at the Department of Mechanical Engineering from Universidade Federal de Minas Gerais. He has published 39 articles in international journals and has presented several research papers at various international conferences held in Brazil and abroad. His research interests include internal combustion engines, alternative energy sources, fuels and combustion.