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Occasionally the journal will include review papers, interviews, and other types of communications. It will be published mainly in English, and at present, there are no page charges.

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INFLUENCE OF FAST PYROLYSIS WITH TEMPERATURE ON GAS, CHAR AND BIO-OIL PRODUCTION

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ABSTRACT

Rice husk is among the products that stand out in use, and it is used as an alternative source of energy. The use of rice husk as biomass in the feeding of pyrolytic reactors for power generation and chemical products can reduce the environmental problem destination of this waste. The advantages of this process are in the proper disposal of this waste and energy generation. Fast pyrolysis of the rice husk was carried out in temperatures of 400-600°C. This work aims to evaluate the influence of temperature on yield and product composition of the gas, bio-oil, and char. The yield of bio-oil proved to be efficient (62 wt.% at 450°C) due to the high heat transfer and mass, as well as the residence time in the reactor. In addition, bio-oil production decreases slightly due to increased gas yield (1 to 15 wt.%) as the temperature increases in the range of 400-600°C, with the composition being severely affected, i.e., The concentration of CO increases and that of CO_2 decreases. In addition, a slight increase in the concentration of CH_4 and C_2-C_4 hydrocarbons occurs with increasing temperature. The yield of char at 400°C and 600°C was 41.14-34.77 wt.%, respectively, corresponding to a decrease of 16 wt.%. The char obtained is of low heating value but has good features for the production of active carbons and amorphous silica. These results demonstrate the efficiency and optimization of the fast pyrolysis of rice husk, in order to obtain biooil
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THE USE OF X-RAY MICROTOMOGRAPHY TO ASSESS CHANGES IN THE VOIDS STRUCTURE OF ROCKS

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ABSTRACT

The oil and gas industry is developing rapidly. Based on this, it is necessary to determine new methods of productive prospecting of mineral deposits. One of the most high-tech and perspective methods is computer X-ray microtomography. For this stage, this method is widely used for the different fields of geology and geophysics. The main advantage is the ability to study the sample without destruction, which is especially important in the process of working with the kern material. In this paper, the method of computerized X-ray microtomography is highlighted. A comparative analysis of the voids structure of an oil source rock before and after exposure to microwave fields using the standard DataViewer software is clarified. As a result of this analysis, an increase in the diameter of a sample of a cylindrical shape after treatment with microwave fields was established, and the formation of microcracks was also established. Based on the results obtained, assumptions were made about the formation of hydrocarbon deposits. In other words, the paper discusses in detail the method that allows fixing changes in the structure of the void space of rocks as a result of oil and gas generation flowing under the influence of wave fields.

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TIME, ENERGY EFFICIENCY IN THE PRODUCTION OF BIODIESEL, AND PRODUCTS DESTINATION IN A BIOREFINERY

DE BONI, Luis Alcides Brandini[1];

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ABSTRACT

This manuscript deals with the production of biodiesel from triglycerides (TG); soybean oil was the primary raw material. The transesterification reaction was used to convert triglycerides into monoalkyl esters. The catalytic mixture of methanol and potassium hydroxide (KOH) was used in the transesterification reaction. The anhydrous refining of biodiesel was used to reduce side reactions during the purification process. The treatment of glycerol by acidification with H3PO4 and its subsequent purification was a convenience process aiming to form the desired byproducts. The

conversion of residual fatty acids to soaps through the saponification reaction or into esters through the esterification reaction with H2SO4 can be done observing the market of those products. The monitoring of the transesterification reaction in real time with laser spectroscopy allows the variation of the temperature during the reaction process without losing the reaction endpoint. The use of only one reaction vessel for the accomplishment of several unit operations aiming the reducing of the reaction time in the production process was well succeeded. The main resulting products are biodiesel, glycerol, fertilizer, and soaps. As expected the biodiesel can be used as a source of energy, the glycerol can be further refined but this process was not explored at this manuscript, the resulting salts can be used as fertilizers, and the soups can be sold and used as a soup.

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ARSENIC SPECIATION IN GROUNDWATER USING THE SOFTWARES PHREEQC, GWB AND GEODELING

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ABSTRACT

Geochemical modelling speciation is used to understand the interactions that occur in the groundwater. Thermodynamic data, kinetic parameters, numerical methods are factors that affect any geochemical modelling system. The conceptual formulation of geochemical modeling calculates the distribution of chemically reactive species for an aqueous solution. The mathematical formulation of the model results in a system of nonlinear algebraic equations that are solved using numerical methods. Most programs allow the user to estimate the speciation model. Activities of aqueous species are usually calculated using the Davies equation, Debye-Hückel equation, or the extended Debye-Hückel equation. We perform a comparative study of geochemical speciation using three different software: PHREEQC^{TM}, Geochemist's Workbench^{TM} (GWB) and GEODELING. Details of each software take into account the distribution, mobility, and availability of chemical species in groundwater. We can observe very similar results in speciation when working with low-temperature systems (20 to 80°C). GWB^{TM}, PHREEQC^{TM}, and GEODELING employ an integrated system to define when to use Davies, Debye-Huckel or Bdot equation, according to the value of the solution ionic strength. The geochemical speciation aimed to compare the results of simulators able to predict the chemical species present in groundwater. The utilization of GEODELING allows comparing the results with software GWB^{TM} and PHREEQC^{TM} with a high degree of acceptance for low temperatures. The numerical methods used by GWB^{TM}, PHREEQC^{TM}, and GEODELING software are able to seek its own best set of numerical solutions to achieve the equilibrium. Users must be cautious when choosing geochemical modeling software, as an essential factor for choosing a simulator is to know the temperature range that will be used.

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TO AUTHORS

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INFLUENCE OF FAST PYROLYSIS WITH TEMPERATURE ON GAS, CHAR AND BIO-OIL PRODUCTION

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ABSTRACT

Rice husk is among the products that stand out in use, and it is used as an alternative source of energy. The use of rice husk as biomass in the feeding of pyrolytic reactors for power generation and chemical products can reduce the environmental problem destination of this waste. The advantages of this process are in the proper disposal of this waste and energy generation. Fast pyrolysis of the rice husk was carried out in temperatures of 400-600°C. This work aims to evaluate the influence of temperature on yield and product composition of the gas, bio-oil, and char. The yield of bio-oil proved to be efficient (62 wt.% at 450°C) due to the high heat transfer and mass, as well as the residence time in the reactor. In addition, bio-oil production decreases slightly due to increased gas yield (1 to 15 wt.%) as the temperature increases in the range of 400-600°C, with the composition being severely affected, i.e., The concentration of CO increases and that of CO_2 decreases. In addition, a slight increase in the concentration of CH_4 and C_2 -C_4 hydrocarbons occurs with increasing temperature. The yield of char at 400°C and 600°C was 41.14-34.77 wt.%, respectively, corresponding to a decrease of 16 wt.%. The char obtained is of low heating value but has good features for the production of active carbons and amorphous silica. These results demonstrate the efficiency and optimization of the fast pyrolysis of rice husk, in order to obtain bio-oil and char.

Keywords: *Biomass, Pyrolysis Conditions, Renewable Energy Potential, Thermal Treatments, Biofuel.*

1. INTRODUCTION

The shortage of fossil fuels has awakened the scientific community for the use of biomass as a source of renewable energy (Carpenter *et al.,* 2014; Demirbas, 2011). A fundamental characteristic of biomass is the possibility of being used as bases in the generation of energy (Mohan *et al.,* 2006).

Rice husk (RH) as biomass energy generation may reduce the environmental problem of the destination of this waste, besides contributing to reducing the use of fuels derived from petroleum. RH discarding is a serious environmental problem due to its properties (difficult decomposition), its constitution (highly phenolic) and the enormous quantity of this material generated annually (Diniz, 2005; Gómez, 2002). The chemical composition of the RH varies according to the type of soil and the main components are cellulose, hemicellulose, lignin, and minerals (Mullen *et al.,* 2009; Moens *et al.,* 2009; Khan *et al.,* 2009; Boateng *et al.,* 2008; Petrus and Noordermeer, 2006).

The inorganic residue contains on average 94-97 wt.% of silica in the hydrated form, totaling from 10 to 30 wt.% of the total husk (Mullen and Boateng, 2009; Boateng *et al.,* 2008). Cellulose is the main component of the cell wall of vegetables and the most abundant organic compound in nature. It consists of a polymer formed of glucose units, through chemical bonds involving oxygen atoms (Huber *et al.,* 2006). The denomination of hemicellulose comprises the non-cellulosic polysaccharides present in the biomass. Generally, they are polymers constituted by monosaccharides of 5 carbon atoms (pentoses) and are therefore known with pentosans. The most frequent component in the pentosan composition is xylan formed by anhydroxylose units (Mullen and Boateng, 2009; Huber *et al.,* 2006). Lignin is a macromolecule chemical that is totally different from cellulose and hemicellulose. The lignin can be represented as a heterogeneous and amorphous polymer whose repeating structural unit is a phenyl propane unit, substituted at various positions on the benzene ring. (Mullen and Boateng, 2009; Huber *et al.,* 2006).

Several conversion technologies (mechanical, biological and thermochemical) have been developed for the exploitation of RH in industry. Thermochemical conversion processes (combustion, gasification, and pyrolysis), the latter has been distinguished by the capacity to produce biofuels in different stages of incorporation. Pyrolysis is a process in which the RH is subjected to a temperature range of 450°C to 750°C in an inert medium. Solid (char), liquid (bio-oil) and gaseous (pyrolytic gas) products are obtained (Meesuk *et al.,* 2011). Bio-oil, a product of fast pyrolysis, can be used as a substitute to fossil fuels and raw material to produce chemicals (Delivand *et al.,* 2011). Fast pyrolysis is a process of thermal decomposition in the absence of oxygen or when the oxygen content is at an incomplete combustion level (Vitali *et al.,* 2013; Zhang *et al.,* 2010). In this thermal conversion process, up to 70% of the biomass energy can be converted into a liquid product (Anex *et al.,* 2010). Great efforts were made to develop new processes for the conversion of biomass into bioenergy (Brown *et al.,* 2013; Bridgwater, 2012).

Fast pyrolysis is a well-studied technology that is reaching an early stage marketing (Jiang and Ellis, 2010; Effendi *et al.,* 2008). The aim of this work is to use rice husk as raw material for the production of bio-oil by fast pyrolysis process in a nitrogen atmosphere, considering a large amount of this material in the form of waste from the world food industry.

Experiments were performed in a tubular furnace and a fixed bed reactor. The chemical composition of the gases and bio-oil was determined using gas chromatography coupled to mass spectrometry. For gas sampling, solid phase microextraction (SPME) was used with polydimethylsiloxane (PDMS)/polyacrylate.

2. MATERIALS AND METHODS

2.1. Raw material

RH was used as raw material, coming from a farm without pre-treatment. The proximate and ultimate analyses of RH are listed in Table 1. The analysis has been carried out in LECO elemental analyzers (CHNS-O) (FlashSmart - Thermo Scientific^{TM}) and thermogravimetric analyzer (TGA-1000 - NAVAS INSTRUMENTS^{TM}), respectively. The calorific value was measured in an isoperibolic calorimeter (C 6000 ISOPERIBOL PACKAGE 1/10 - IKA^{TM}). The chemical composition of ash (Table 2), including silica and major metal compounds, was determined by X-ray fluorescence (S6 JAGUAR EasyLoad – Bruker^{TM}).

2.2. Pyrolysis experimental procedure

The system consists of a vessel equipped with a vertical shaft connected to a piston placed below the bed of the material and allows the continuous feeding of up to 100 g/hour of RH. Nitrogen has been used as an inert gas with a flow rate of 20 L/min. The total height of the reactor is 42 cm, the conical section is 25 cm, and the angle of the conical section is 35°. The diameter of the cylindrical section is 15 cm, the bottom diameter is 2.5 cm, and the gas inlet diameter is 1.25 cm.

The volatiles products leave the reactor together with the inert gas and pass through a forced convection oven maintained at 300°C, which prevents the condensation of heavy compounds. In addition, the residence time of the generated vapors is in the range of seconds, avoiding the cracking of the vapors before their condensation. Thus, the liquid collected in the condenser is primarily the aqueous phase of the bio-oil, while the heavier compounds forming the organic phase are retained in the filters. To study the effect of the pyrolysis temperature on the characteristics of the product, the pyrolysis tests were performed at 400, 450, 500, 550 and 600°C. The tests were carried out in continuous mode feeding 1 g/min of biomass.

2.3. Product analysis

Volatiles leaving the reactor were analyzed with a gas chromatograph (Perkin Elmer^{TM}). The reactor output is diluted with an inert gas to ensure that all volatile products formed during pyrolysis enter the chromatograph and are analyzed. The liquid product identifications were performed in a gas chromatograph, and char has been characterized by means of elemental and proximate analysis and higher heating value.

3. RESULTS AND DISCUSSION

3.1. Product yields

The pyrolysis products were grouped into three different fractions: gas fraction, liquid (bio-oil) and char. The evolution with the temperature of the yields of these fractions (on wet basis) is shown in Figure 1.

Bio-oil is the main fraction of the product in all temperature ranges studied, with the maximum yield at 450°C. In general, as the pyrolysis temperature increases, we also observe an increase in the gas yield, due to the efficiency of the secondary cracking in the pyrolysis vapors. The drop in char yield becomes more pronounced between 400 and 450°C. The high yield of bio-oil obtained (62.10 wt.% at 450°C) shows the good performance of the fast pyrolysis of RH due to the high rates of heat transfer and mass, which promote devolatilization reactions, and the short residence times the volatiles, which minimize the cracking of these components. (Kabir and Hameed, 2017; Damartzis and Zabaniotou, 2017; Naqvi *et al.,* 2014; Alavrez *et al.,* 2014; Abu Bakar and Titiloye, 2013). The high char yield (41 wt.% at 400°C) is due to the high ash content in RH. The main responsible for this behavior of RH is in the textural properties, thin layers composed of cellulose, hemicellulose and lignin (Hossain *et al.,* 2017; Naqvi *et al.,* 2015; Yu *et al.,* 2016; Tripathi *et al.,* 2016; Angin, 2013; Ertaş and Hakkı Alma 2010). Thus, the devolatilization rate of each particle will be extraordinarily high, favored by the nitrogen flow in the pyrolysis reaction environment. Such conditions promote the rapid devolatilization of this residue, which gives rise to high yields of bio-oil in the 400-600°C range. (Tripathi *et al.,* 2016; Tripathi, Sahu and Ganesan 2016; Stefanidis *et al.,* 2011).

3.2. Gas composition

The gas fraction is composed mainly of carbon dioxide and carbon monoxide (Figure 2). The yields increase with temperature due to the increase in decarboxylation and decarbonylation reactions (Zhang, 2016; Ding *et al.,* 2016; Zhang *et al.,* 2015; Naqvi 2012; Wang *et al.,* 2013; Artes, 2012).

In addition, this fraction is also composed of small amounts of hydrocarbons (C_2-C_4). As observed in Figure 2, the concentration of CO increases with temperature, while that of CO_2 decreases. This is because at temperatures below 450°C the decarboxylation reactions prevail, but at temperatures above 450°C the main secondary reactions are those of decarbonylation, and therefore the release of CO is greater (Tripathi *et al.,* 2016; Tripathi, Sahu and Ganesan 2016). The yield of light hydrocarbons (C_2-C_4) and H_2 also increases with temperature due to cracking reactions. These non-condensable gases are of the low energy value in a pyrolysis process due to dilution with the entrainment gas (N_2). In addition, the low CO_2 yield at 600°C is a favorable environmental feature involving the RH pyrolysis process (Stefanidis *et al.,* 2011).

3.3. Bio-oil composition

The bio-oil compounds were in Table 3 according to functional groups together with the major individual compounds. Oxygenated compounds (phenols, cyclopentenones, furans, ketones, aldehydes, carboxylic acids) make bio-oil unstable and reduce miscibility with hydrocarbons and calorific value (Bridgwater, 2012; Heo *et al.,* 2010). In addition, the heterocyclic compounds of the bio-oil make it viscous and easy to polymerize (Heo *et al.,* 2010-1). The water content in the bio-oil is slightly affected by the pyrolysis temperature since its yield remains in the range of 25 to 27 wt.%. As noted in Table 3, the major organic compounds in the bio-oil are phenols, which are formed on the decomposition of lignin macromolecules above 350°C, and their yields increase considerably at 600°C (33 wt.%). (Chiaramonti *et al.,* 2007; Lu et al., 2009; Lu *et al.,* 2008; Park *et al.,* 2008). The high yield of phenolic compounds in the bio-oil is consistent with other literature results for the rapid pyrolysis of RH. (Li *et al.,* 2012; Lu *et al.,* 2011). Ketones are the second largest organic group in the bio-oil. As observed in Table 5, both groups decrease with temperature, especially at 600°C. Ketones are formed by condensation reactions of the fraction derived from carbohydrates and decomposition of the various oxygenates and furans (Jacobson *et al.,* 2013; He and Wang, 2012; Bulusheva and Rossa, 2011; Peterson *et al.,* 2008; Mohan *et al.,* 2006).

When the pyrolysis temperature is increased, cracking reactions are more severe and lighter compounds are formed (Graça *et al.,* 2013). Ketones are present in nature and are synthesized for many applications. They are mainly used as solvents and intermediates in the chemical industry (Mansur *et al.,* 2013; Shiramizu and Toste, 2012; Honnery *et al.,* 2008; Stamatov *et al.,* 2006).

Acid functional groups have their highest yield at the temperature of 450°C (9.89 wt.%), and the main compound of this group is acetic acid. These compounds are formed by the thermal decomposition of constituent components in RH, and the presence of acetic acid is specifically attributed to the deacetylation of hemicelluloses (Zheng, 2007; Mohan *et al.,* 2006; Uzun *et al.,* 2006; Özbay *et al.,* 2006). The presence of these carboxylic acids is responsible for the strong acidity of this bio-oil (pH in the 2.5–3.5 range) (Graça *et al.,* 2013; He and Wang, 2012; Mortensen *et al.,* 2011; Wildschut, 2009). They can cause corrosion in subsequent processing when the equipment is made of poor quality material. In addition, organic acids are valuable by-products after separation. Therefore, the removal of acids is important for the use of bio-oil as an intermediary in the production of fuels and chemicals (Elliot *et al.,* 2009; Huang *et al.,* 2009; Onay, 2007).

3.4. Char characterization

Evolution of physical, chemical, structural and morphological properties has been analyzed at different pyrolysis temperatures. The results are summarized in Table 4. The proximate analysis shows that the volatiles and the fixed carbon content in the char decrease as the temperature is increased, which is explained by the higher ash content in the residue (Pecha and Garcia-Perez, 2015; Paulsen Patwardhan *et al.,* 2010, Lehmann and Joseph, 2009). This conclusion is also reflected in the elemental analysis because the total carbon content is also lower when the temperature is elevated. The main consequence of the high ash content is that the calorific value of char decreases as the pyrolysis temperature is increased (Zhou, 2013; Mayes and Broadbelt, 2012; Mamleev *et al.,* 2009). Ash yields obtained in the pyrolysis of other lignocellulosic residual materials are lower, generally below 5 wt.%. In view of these results, it can be concluded that the combustion of this char is an undesirable option due to the large amount of ash that must be handled, which causes serious environmental and health problems (Hawash *et al.,* 2017; Sadaka *et al.,* 2014; Yanik *et al.,* 2007; Bogale, 2009). In addition, the calorific value (18.7 MJ/kg for char obtained at 400°C) is low when compared to other solid fuels, such as lignite (28 MJ/kg) or coke (29 MJ/kg) (Fairous, 2009; Oasmaa and Kuoppala, 2003). As noted in Table 4, BET surface areas are low (12-41 m^2/g), and macro and mesopores are formed primarily at 400°C, and microporosity is created in the material as the pyrolysis temperature is raised. In fact, the surface area depends on the mass of carbon removed during pyrolysis, creating pores in the material whose size increases as the temperature is increased (Zhaoying *et al.,* 2018; Hasan Khan Tushar *et al.,* 2012; Shen *et al.,* 2009).

Therefore, upgrading this by-product of activated carbon waste will improve the BET surface areas, and therefore a valuable material will be obtained with good adsorption properties for water and sewage treatment (Chen *et al.,* 2011). Furthermore, due to its high silica content, rice husk ash can be an economically viable feedstock for the production of silicates (An *et al.,* 2011). Amorphous silica can be extracted with alkaline compounds such as sodium hydroxide or sodium carbonate (Adam *et al.,* 2012).

4. CONCLUSIONS

Fast pyrolysis of RH, used in this study, achieved favorable yields of bio-oil, as well as the reduction of char. These results are due to the high rates of heat and mass transfer and to the reduced permanence time of the volatiles in the reaction system. The maximum yield of bio-oil (62.10 wt.%) was obtained at 450°C, with low gas yield (2.21 wt.%). It should be noted that a temperature increase between 400 and 600°C range leads to a small reduction in the production of bio-oil, whose composition is slightly modified by increasing the concentration of phenolics, furans, and the reduction of acids and ketones. The gas yields increase from 1 to 15 wt.% as the temperature increases in the 400-600°C range, with the composition being severely affected, i.e., the concentration of CO increases and that of CO_2 decreases. In addition, a slight increase in the concentration of CH_4 and C_2 -C_4 hydrocarbons occurs with increasing temperature. The char yield at 400°C and 600°C range was 41.14 - 34.77 wt.% respectively, corresponding to a decrease of 16 wt.%. The char obtained is of low heating value but has good features for the production of active carbons and amorphous silica. In addition, the production of amorphous silica by rapid pyrolysis of RH is an attractive alternative to conventional methods, such as combustion and solvent treatments.

5. ACKNOWLEDGMENTS

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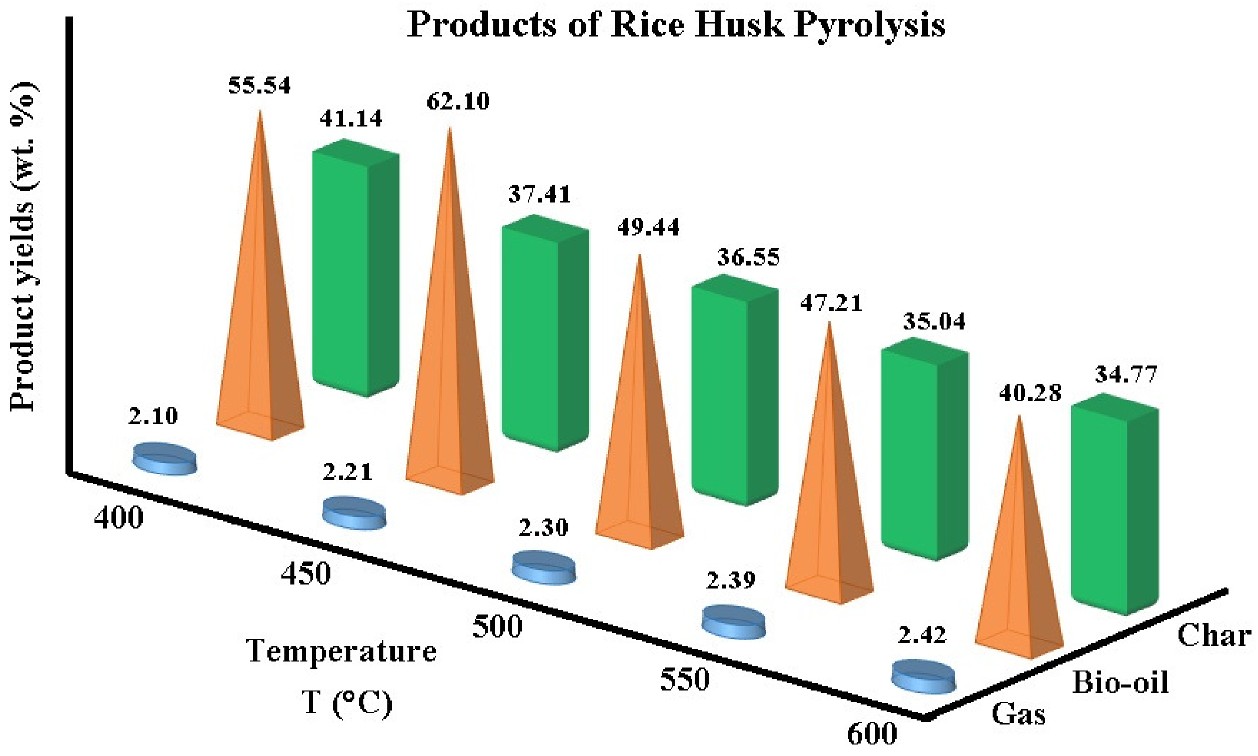

Figure 1. *Effect of temperature on the product yields in RH pyrolysis*

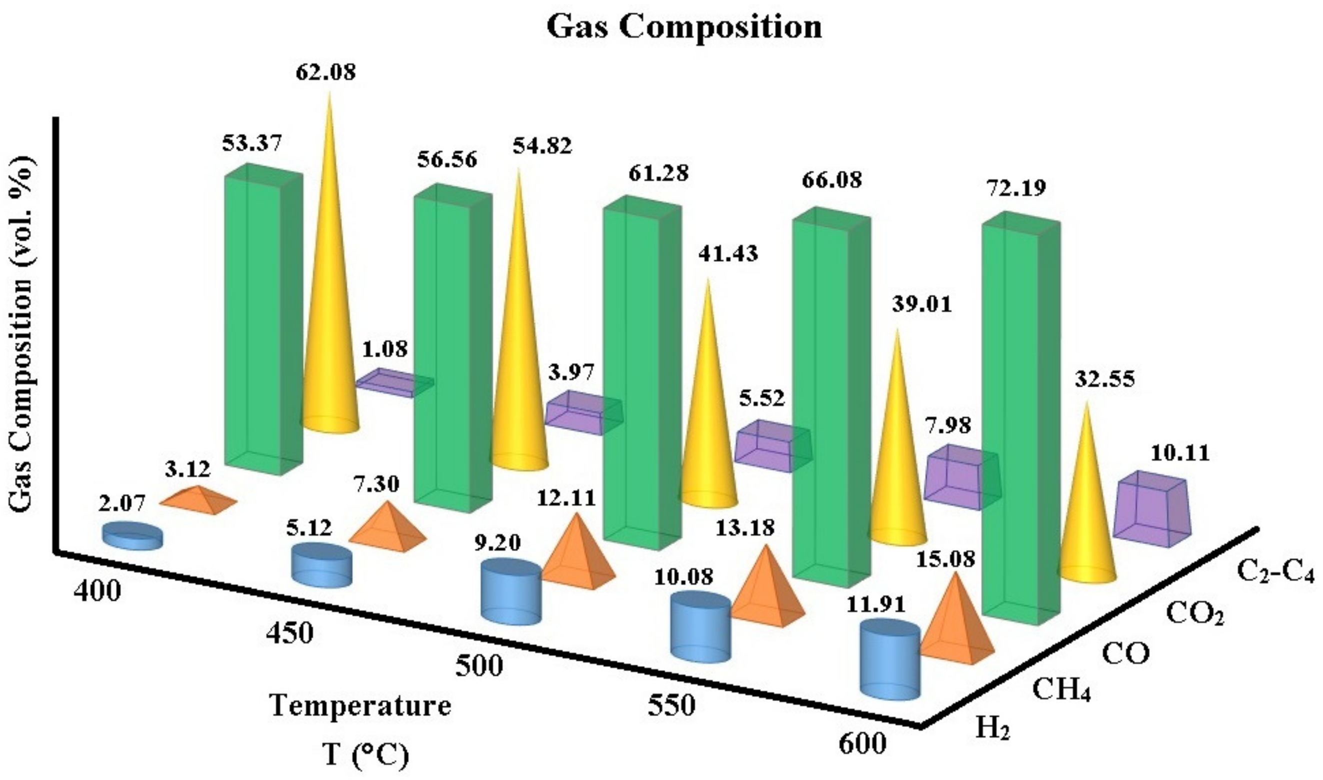

Figure 2. *Influence of temperature on gas composition*

Table 1. *Properties of the RH*

Proximate analysis		**Ultimate analysis**	
Parameters	**Weight (%) on dry basis**	**Elements**	**Weight (%) on wet basis**
Volatile matter	74.8	Carbon	48.5
Fixed carbon	18.91	Hydrogen	6.92
Ash	13.42	Nitrogen	0.75
Moisture	1.94	Oxygen	40.11
HHV* (MJ/kg)	19.51		

*HHV: Higher Heating Value

Table 2. *Chemical composition of the RH ash*

Compound	**Weight (%)**
SiO_2	97.92
Al_2O_3	0.41
Fe_2O_3	0.19
MnO	0.01
MgO	0.13
CaO	0.33
Na_2O	0.15
K_2O	0.29
TiO_2	0.03
P_2O_5	0.10
Others	0.22

Table 3. *Yields of the main chemical compounds in the bio-oil*

Compounds	**400°C**	**450°C**	**500°C**	**550°C**	**600°C**
Acids	8.26	9.89	8.22	7.67	6.65
Acetic acid	2.45	3.51	2.39	2.49	2.61
Propanoic acid	1.49	0.95	0.30	0.30	0.31
Aldehydes	1.96	2.49	2.26	2.34	2.38
Formaldehyde	0.31	0.48	0.50	0.52	0.59
Ketones	9.88	9.06	8.62	5.99	4.73
1-Hydroxy-2-propanone	1.63	1.36	0.92	0.74	0.44
1,3-Cyclopentanedione	3.24	2.75	2.67	1.96	0.84
2-3-methyl-2-cyclopentenone	1.23	1.22	1.42	1.35	0.43
Phenols	10.11	10.63	10.28	11.57	13.42
Alkyl-phenols	3.16	3.84	3.89	4.08	6.82
Guaiacols	4.03	3.42	2.93	2.89	2.82
Catechols	2.99	3.44	3.53	3.61	3.88
Ethers	3.12	3.11	2.76	2.98	3.12
2,2,4-Trimethyl-1,3-dioxalane	2.48	2.37	1.70	1.57	1.00
Carboxylic Anhydrides	1.23	1.12	1.04	1.11	1.13
Furans	4.53	4.79	5.28	5.00	4.37
Nitrogenated compounds	1.11	1.40	1.66	1.38	1.14
Water	27.13	25.02	25.28	25.37	25.99

Table 4. *Influence of pyrolysis temperature on char properties.*

Char properties	**400°C**	**450°C**	**500°C**	**550°C**	**600°C**
Proximate analysis (wt.%)					
Volatiles	22.4	18.6	19.0	13.8	15.1
Fixed carbon	49.6	44.4	43.8	41.1	45.9
Ash	42.9	55.7	57.1	56.2	58.2
Ultimate analysis (wt.%)					
Carbon	55.4	54.3	54.0	53.8	52.3
Hydrogen	2.9	2.8	2.5	2.4	2.0
Nitrogen	0.8	0.7	0.5	0.5	0.5
Oxygen	12.5	3.8	5.9	3.0	2.7
C/H	2.4	2.5	3.1	3.4	3.8
Low Heating Value (MJ/kg)	18.7	16.8	16.0	15.4	14.7
Surface properties					
BET surface (m^2/g)	12.1	17.3	28.9	32.0	41.1
Average pore diameter (Å)	110.5	124.4	85.1	83.8	82.5
Pore volume (cm^3/g)	0.031	0.034	0.061	0.062	0.062

SOUTHERN BRAZILIAN
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THE USE OF X-RAY MICROTOMOGRAPHY TO ASSESS CHANGES IN THE VOIDS STRUCTURE OF ROCKS

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ABSTRACT

The oil and gas industry is developing rapidly. Based on this, it is necessary to determine new methods of productive prospecting of mineral deposits. One of the most high-tech and perspective methods is computer X-ray microtomography. For this stage, this method is widely used for the different fields of geology and geophysics. The main advantage is the ability to study the sample without destruction, which is especially important in the process of working with the kern material. In this paper, the method of computerized X-ray microtomography is highlighted. A comparative analysis of the voids structure of an oil source rock before and after exposure to microwave fields using the standard DataViewer software is clarified. As a result of this analysis, an increase in the diameter of a sample of a cylindrical shape after treatment with microwave fields was established, and the formation of microcracks was also established. Based on the results obtained, assumptions were made about the formation of hydrocarbon deposits. In other words, the paper discusses in detail the method that allows fixing changes in the structure of the void space of rocks as a result of oil and gas generation flowing under the influence of wave fields.

Keywords: *X-ray microtomography, oil shale, digital petrophysics, oil generation, Bazhenov suite.*

1. INTRODUCTION

Currently, there is an epoch of transition from traditional (exhaustible) energy resources, most of which are various types of hydrocarbon compounds concentrated in the subsoil, to renewable energy sources: atomic, solar and wind energy. This is due to natural, technological progress.

However, the problem lies in the fact that technological progress has not yet provided people with the necessary amount of renewable energy, and hydrocarbon reserves concentrated in standard deposits are decreasing every year. These data indicate the need to develop an innovative type of technology that is capable of extracting oil from clay-bitumen oil source deposits on the one hand and, on the other hand, to ensure a smooth transition from traditional energy sources (hydrocarbons) to alternative (thermonuclear fusion, superconductors).

In this paper, the author will discuss a particular case of studying radical reactions caused by the nuclear-electron interaction of isotopes with an angular electron magnetic effect [1-3]. In other words, a method will be highlighted in the paper that allows one to record changes in the structure of the oil source rock voids as a result of oil and gas generation occurring under the influence of wave fields, in this case, electromagnetic waves of ultrahigh-frequency (microwaves). The methodical part of the work will consist in the approach of the comparative analysis of the data on the structure of the rock structure obtained on the X-ray computer microtomograph SkyScan 1172 before and after the treatment with microwaves. The principles of scanning, reconstruction,and analysis of tomographic data will be clarified in detail, and the conclusions will be made on the basis of the results obtained about the processes occurring during the formation of hydrocarbon deposits.

2. MATERIALS AND METHODS

The object of research is the change in the structure of a sample of an oil source rock, in this case, the black mudstone of the Bazhenov suite (Russia, Western Siberia) as a result of radical reactions in dispersed organic matter (kerogen) [4-9]. As a consequence of microwave treatment, oil and gas generation processes occur, with a natural increase in the volume of hydrocarbons during the transition from a solid state (kerogen) to a liquid (oil) and gaseous (gas). During this process, the structure of the voids changes due to the cracking of the rock under the action of the high pressure of newly formed fluids.

Based on these data, an assumption was made that the existence of oil and gas generation processes or radical reactions in dispersed organic matter can be assessed not only by geochemical methods of comparative analysis, for example, by Rock-Eval or by chromatographic analysis of the composition of the bitumen, but also by computer X-ray microtomography with a resolution of samples shooting of about 3 micrometers per pixel. The experimental technique consists in a comparative analysis of the structure of the voids of a sample in its natural state (without thermal and wave processing) and the modified structure of the voids of a sample subjected to microwave treatment (thermal and wave processing).

Comparative analysis is carried out objectively, due to the excellent function of the software of the SkyScan microtomographs. The DataViewer program makes it possible to accurately overlap tomographic slices of samples before and after microwave treatment [10].

The duration of the microwave treatment of the sample was 8 minutes, with a marked increase in the sample temperature.

The method of computer X-ray microtomography is based on obtaining a set of shadow projections of the sample from different sides, after which these shadow projections using specialized software, in this case, the NRecon program, are reconstructed into tomographic sections, usually presented in 8-bit format with the graduation of the X-ray density of the sample in grayscale from black to white or vice versa [11].

The principle of operation of the method of microtomography (see Figure 1) is the same with medical tomography or tomography for a full-sized core. It is important to note the geometrical dimensions of the sample – the smaller the sample, the higher the resolution and less noise (typical of the SkyScan 1172 microtomograph). In this case, the golden mean was chosen: the sample diameter was 12 mm, and the shooting resolution was 3.3 µm/pixel. Also, when conducting high-resolution sampling, it is necessary to select the correct parameters: the type of filter, the scan step and the number of frames. In this case, the following parameters were selected from the microtomograph experience: filter – aluminum + copper (standard), scanning step – 0.3 degrees, number of frames – 5, number of random frames – 30, scanning was performed at 360 degrees. Choosing the right number of random frames and scanning at 360 degrees helps to avoid ring artifacts.

After the tomographic projections of the sample were obtained, they were reconstructed with the following parameters: Smoothing=3; Smoothing kernel=0 (Asymmetrical boxcar); Ring Artifact Correction=20; Object Bigger than FOV=ON; Filter cutoff relative to Nyquist frequency=100; Filter type=0; Filter type description=Hamming (Alpha=0.54); Undersampling factor=1; Threshold for defect pixel mask (%)=0; Beam Hardening Correction (%)=46; Minimum for CS to Image Conversion=0.000000; Maximum for CS to Image Conversion=0.100000. An example of the obtained qualitative tomographic slice is shown in Figure 2.

After carrying out experiments and obtaining digital models of core samples before and after treatment with microwave waves, the samples were processed using the capabilities of the DataViewer program. A logical “difference image” operation was performed between digital models – the difference is an image; a more detailed algorithm of the operation is presented in the guidelines of the device manufacturer [12].

3. RESULTS AND DISCUSSION:

As a result of the research, the following materials were obtained, see Figure 3. The yellow arrows indicate the fracturing resulting from those radical reactions and oil and gas generation processes. An increase in the diameter of the sample is also clearly observed; this is indicated by the light line along the contour of the sample (for convenience, it is outlined nearby with green). Numerous black dots, next to which white dots are combined, indicate the impossibility of joining heavy mineral inclusions of the sample. In the end, most of the image is grey; it indicates the successfully combined parts of the sample.

In general, the literary analysis showed that the cracking of organic matter significantly changes the structure of the voids [13-16]. As a rule, the degree of change in the structure of the voids depends on many factors: the degree of maturity of organic matter (kerogen), the rate of thermal effects on the rock, volume fraction of kerogen and others [17]. However, an important feature of this study is a systematic explanation of the essential features of the X-ray microtomography method, which make it possible to reasonably use comparative analysis before and after conducting an experiment on a test sample.

Based on the data obtained, it can be noted:

Indirectly, the computerized X-ray microtomography method can be used to assess the progress of the distribution of kerogen (the approach works in the absence of carbonate inclusions in the sample).

As is well known, cracks propagate along the path of least resistance; objectively, it should be noted that in this experiment most of the cracks formed only in the marginal parts, and the cracks are practically not observed in the central part. This may be a confirmation of the ideas of Nesterov that pressure inhibits chemical reactions, and in order to overcome the energy barrier, it is necessary to carry out pressure relief [18]. Perhaps as a result of microwave treatment and thermal heating, radical reactions proceeded more actively in the edge parts of the sample than in the central part. In this case, these studies can help explain the abnormally high pressures in low-permeability reservoirs – Achimov deposits, and will also be consistent with the presence of fracture on the wings of deposits.

There are many opinions about the processes of formation of hydrocarbon deposits. The most common is the opinion on thermobaric conditions, i.e., upon reaching specific temperatures (about 300 degrees Celsius) and pressure, the dispersed organic matter begins to generate liquid and gaseous hydrocarbons. This is all confirmed by numerous laboratory experiments, but for some reason, everyone forgets that there are no such temperatures in oil source rocks and there have never been. In this regard, it is possible to agree with the opinion of the correspondent member of the Russian Academy of Sciences I.I. Nesterov that the processes of petroleum generation proceed discretely and most likely the most important role is played by isotopes with an angular electron magnetic effect, on which Anatoly Leonidovich Buchachenko has devoted many works. [19, 20]

4. CONCLUSIONS

The technique of using a comparative analysis of the results of the computerized X-ray microtomography method of the core was used to identify the qualitative characteristics in the structure of the voids of the samples before and after exposure to microwave waves. The obtained results were interpreted and backed up by the judgments of the leading Russian scientists Nesterov and Buchachenko.

As a result of the research, one can draw the following conclusions:

1. The method of computer microtomography is recommended for use in tasks related to the study of the voids of rock samples.
2. It is recommended to conduct additional research in this direction since information is presented only for one experimental sample.
3. The fact of an increase in the diameter of a sample of a cylindrical form of black mudstone of the Bazhenov suite as a result of 8-minute treatment with microwave radiation was recorded.

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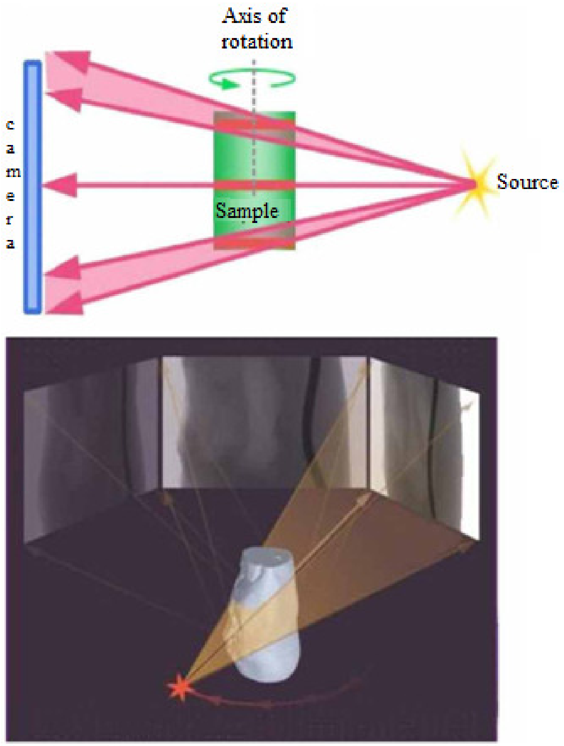

Figure 1. *The principle of the SkyScan 1172 microtomograph operation*

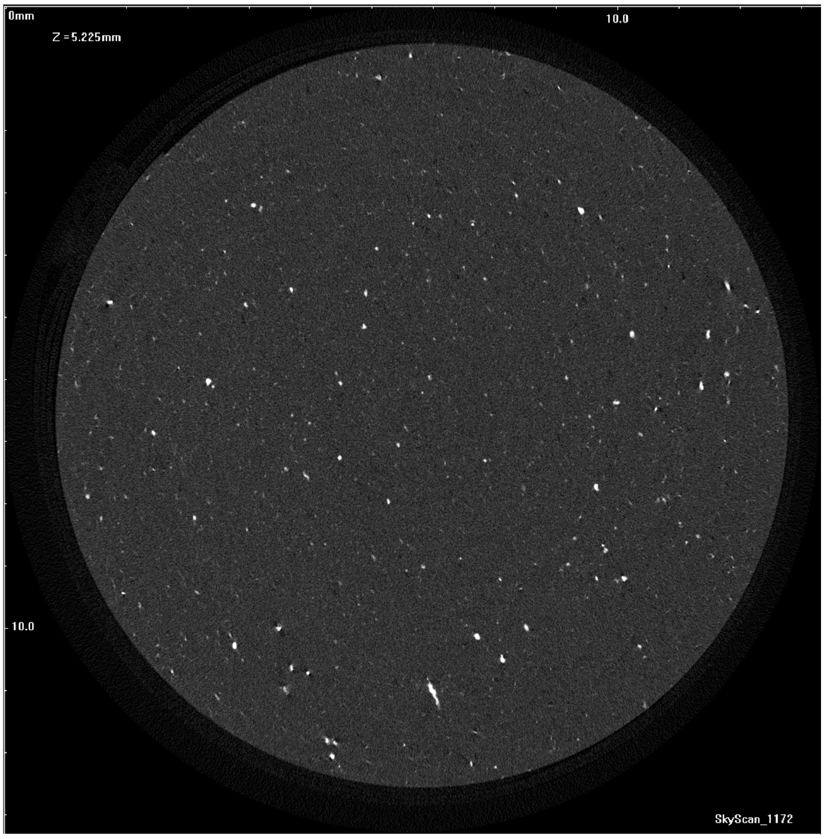

Figure 1. *An example of a qualitative tomographic slice*

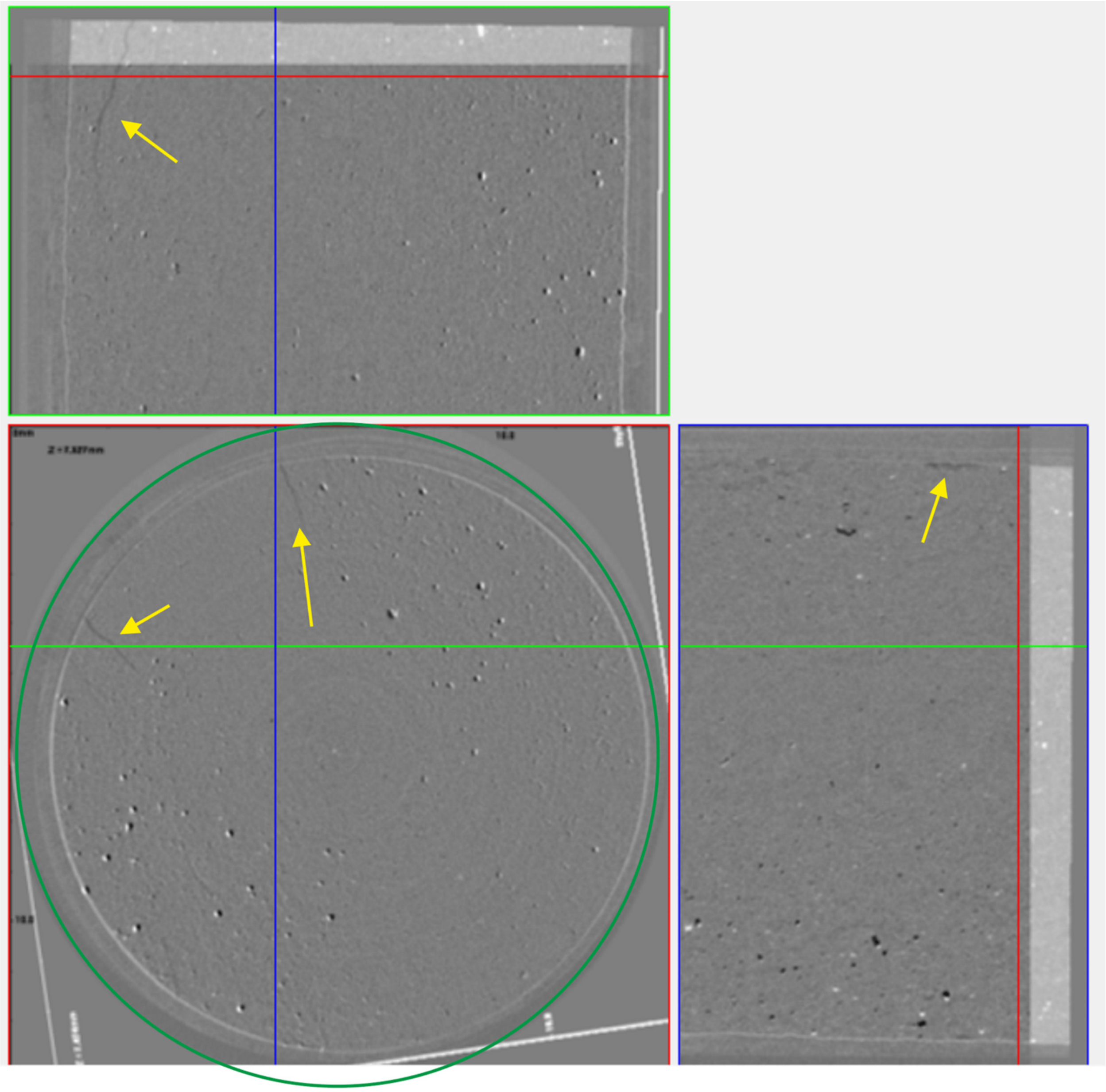

Figure 2. *Orthogonal sections of the combined digital model after performing the logical operation "difference image" (before and after exposure to microwave)*

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TIME, ENERGY EFFICIENCY IN THE PRODUCTION OF BIODIESEL, AND PRODUCTS DESTINATION IN A BIOREFINERY

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ABSTRACT

This manuscript deals with the production of biodiesel from triglycerides (TG); soybean oil was the primary raw material. The transesterification reaction was used to convert triglycerides into monoalkyl esters. The catalytic mixture of methanol and potassium hydroxide (KOH) was used in the transesterification reaction. The anhydrous refining of biodiesel was used to reduce side reactions during the purification process. The treatment of glycerol by acidification with H3PO4 and its subsequent purification was a convenience process aiming to form the desired byproducts. The conversion of residual fatty acids to soaps through the saponification reaction or into esters through the esterification reaction with H2SO4 can be done observing the market of those products. The monitoring of the transesterification reaction in real time with laser spectroscopy allows the variation of the temperature during the reaction process without losing the reaction endpoint. The use of only one reaction vessel for the accomplishment of several unit operations aiming the reducing of the reaction time in the production process was well succeeded. The main resulting products are biodiesel, glycerol, fertilizer, and soaps. As expected the biodiesel can be used as a source of energy, the glycerol can be further refined but this process was not explored at this manuscript, the resulting salts can be used as fertilizers, and the soups can be sold and used as a soup.

Keywords: *transesterification, real-time LASER spectroscopy, byproducts, energy efficiency.*

1. INTRODUCTION

Let us assume that you have some previous knowledge about the biodiesel industry and let's explore some possibilities in how to make a production facility more productive and lucrative. To get acquainted with this type of industry lets do a quick review of some of the process involved in the biofuel industry.

It is suggested the reading of the references about transesterification [1-5], about esterification [6-10], about saponification [11-15], about acidification and neutralization reactions [16-20], monitoring of chemical reactions in real time [21-25].

The transesterification reaction is the process used to convert an ester into another ester by the exchanging the organic group R″ of an ester with the organic group R′ of alcohol. This reaction is catalyzed by the addition of a base catalyst. Figure 1 summarizes the transesterification reaction [1-5]. The transesterification reaction was chosen as the primary reaction in the production process of this chapter.

The esterification reaction is used to produce esters when the starting products are not esters. When carboxylic acids are heated in the presence of alcohols and an acid catalyst, usually concentrated sulphuric acid (H_2SO_4 95.0-98.0%), the reaction products are esters, water, and the residue of the catalyst. Figure 2 summarizes the esterification reaction [6-10].

The saponification reaction is used to produce soap, and it is possibly an interesting alternative to treat the residues of biodiesel production. Figure 3 summarizes the saponification reaction [11-15].

The acidification and neutralization reactions [16-20] may be used to convert residual soaps into free fatty acids (FFA) and to neutralize the catalyst respectively.

The monitoring of chemical reactions in real time with LASER spectroscopy [21-25] can be done with a setup equivalent to Figure 5. This technique is used to determine the endpoint of the transesterification reaction and follows its kinetics trough time.

2. MATERIALS AND METHODS

Suppose that you have at your disposal a reactor, similar to the one in Figure 6. It is not relevant that the components of the reactor are inside or outside the reactor, in any of the cases, there shall be pros and cons to consider, and you should evaluate what will suit you better.

2.1 DEVELOPMENT

The present experiments were conducted in the laboratory, and the lab results were scaled up to the proposed reactor. Commercial soybean oil (triglyceride), potassium hydroxide (catalyst) and methanol (alcohol) were used. The chemical reaction that occurred in the reactor was transesterification, followed by acidification, esterification or saponification. Suppose that you will operate the reactor of Figure 6 according to the procedures below.

Considering Figure 7, the generalized aspects of the system and the following operations are carried out to produce biodiesel in this reactor:

1. Whereas, the catalyst is prepared in the mixer vessel (6) of Figure 7. Add the volume of methanol contained in the vessel 5 of Figure 2 to the reactor. For this experiment it was used 130ml;
2. By titration, determine the mass of the catalyst, stored in the vessel (4) of Figure 7, to be used;
3. Add the catalyst (KOH) to the methanol, in this case, and it was used approximately 10g;
4. Dissolve the catalyst in methanol for *in situ* production of the catalytic mixture;
5. Add the oil to the reactor;
6. Activate the reactor agitation system;
7. Turn on the reactor heating system. The initial oil temperature was 20,64 °C (69.15 F);
8. Activate the reaction monitoring system(real-time LASER spectroscopy);
9. Under constant stirring add the previously prepared catalytic mixture to the reactor. (Date of acquisition of the data 9/27/2011 Time that the first transesterification reaction started: 10:55:57 HH:MM: SS. The end of the monitoring time: 12:58:37 HH:MM: SS. The total amount of samples was 7082 points. Total obtained data: 63738 points. Total monitoring time: 2:02:40 HH:MM:SS)
10. Allow the reaction to proceed with increasing temperature until the chemical equilibrium is established by the monitoring system (graphic example in Figure 8). The temperature at the chemical equilibrium was 57.31 °C (135.16 F);
11. After the reaction reaches chemical equilibrium, turn off the stirring system and heating system;
12. Activate the electrostatic separation system;
    a) Simultaneously initiate the preparation of the catalytic mixture for the second transesterification reaction.
    b) Repeat steps 1-4 by adjusting the volume of the reagents to 26 ml of methanol and 2 g of KOH.
13. Allow the separation of glycerin and biodiesel;
14. Separation of the glycerin is readily determined by the optical system, a sharp variation in absorbance indicates that the glycerin has been separated (example in Figure 3);
15. After the glycerin separation from the biodiesel phase, turn off the electrostatic separation system;
16. Move the glycerin into the vessel 15 of Figure 7;
17. Maintain the product of the first transesterification reaction in the reactor. Believe that it's purity is not less than 80% conversion of raw material into fuel or make a *H^1NMR* test to confirm (De Boni *et al.*, 2013)
18. Activate the reactor agitation system;
19. Start the heating system of the reactor. The initial temperature in the second transesterification reaction was 39.01 °C (102.21 F);
20. Activate the reaction monitoring system;
21. Under constant stirring add the previously prepared catalytic mixture to the reactor. (Date of acquisition of the data 27/9/2011 Time that the second transesterification reaction started: 13:09:35 HH:MM:SS. The end of the monitoring time: 14:32:38 HH:MM:SS. The total amount of samples was 4798 points colected. Total obtained

data: 43182 points. Total monitoring time: 1:23:03 HH:MM:SS);

22. Allow the reaction to proceed, with the elevation of temperature, until the chemical equilibrium is established by the monitoring system (graphic example in Figure 9). The temperature at the chemical equilibrium was 56.31 °C (133.36 F);
23. After the reaction reaches the second chemical equilibrium, turn off the stirring and heating system;
24. Activate the electrostatic separation system
    a) Simultaneously initiate the preparation of the catalytic mixture for the third transesterification reaction.
    b) Repeat steps 1-4 by adjusting the volume of the reagents to 5 ml of methanol and 0.4 g of KOH.
25. Allow the separation of glycerin and biodiesel;
26. Separation of the glycerin is readily determined by the optical system, a sharp variation in absorbance indicates that the glycerin has been separated (example in Figure 5);
27. After the glycerin separation from the biodiesel phase, turn off the electrostatic separation system;
28. Conducting the glycerin into the vessel 15 of Figure 7;
29. Maintain the product of the second transesterification reaction in the reactor. Believe that it's purity is not less than 96% of conversion of raw material into fuel.
30. Activate the reactor agitation system;
31. Activate the reactor heating system. The initial temperature in the third transesterification reaction was 32,02 °C (89.63 F) (Figure 10);
32. Activate the reaction monitoring system
33. Under constant stirring add the previously prepared catalytic mixture to the reactor (Date of acquisition of data 27/9/2011. The time that the third transesterification reaction started: 14:40:05 HH:MM:SS. The end of the monitoring time was 16:48:13 HH:MM:SS. The total amount of samples was 7397 points. Total obtained data: 66573. Total monitoring time: 02:08:08 HH:MM:SS);
34. Allow the reaction to continue, with the elevation of temperature, until the chemical equilibrium is established by the monitoring system (there is a graphical example in Figure 6). The temperature at the chemical equilibrium was 56,05 °C (132.8 F);
35. After the reaction reaches the second chemical equilibrium, turn off the stirring and heating system;
36. Activate the electrostatic separation system;
37. After the glycerin separation from the biodiesel phase, turn off the electrostatic separation system;
38. Conducting the glycerin into the vessel 15 of Figure 7;
39. Maintain the product of the third transesterification reaction in the reactor. Believe that its purity is not less than 99% conversion of raw material into fuel.
40. Switch on the stirring system
41. Turn on the low-pressure system;
42. Use the flash distillation system;
43. Remove the residual alcohol present in the biofuel, reserving the same for later reuse;
44. After completion of alcohol withdrawal, switch off the low-pressure system and stop using flash distillation;
45. Add under constant stirring, the cleaning agent to initiate refining process (for this example, use the sorbent of your choice or availability on the local market as *Magnesol*®, *Eco2Pure*®, *Amberlite*®, *Purolite*®*,* or another type of clay);
46. Allow interaction of the biofuel with the refining agent;
47. After the refining/cleaning agent has completed its purpose, activate the recirculation filtration system;
48. After the filter has wholly removed the cleaning agent, transport the fuel fluid to a suitable container (Figure 7, vessel 14);
49. Clean the filter as necessary.
50. To treat the crude glycerol of vessel 10, at the proper moment, when the reactor (11) is empty move the content of vessel 10 to vessel 11. Add phosphoric acid from vessel 17. This will acidify the medium producing a salt (K_3PO_4) that can be placed in vessel 12. Free fatty acids that can be placed in vessel 9, and yellow glycerol that is moved to vessel 15. The yellow glycerol can pass further treatment to be sold as distilled glycerol, but it will not be explored in this chapter.
51. The FFA from vessel 9 can be converted into biodiesel or soap, depending on what is the best economic opportunity. To convert the FFA into biodiesel, the content of vessel 9 is moved to vessel 11. An esterification reaction will take place,

mixing the alcohol from vessel 5 with the sulfuric acid of vessel 16 in the vessel for the preparation of catalyst (6). This catalytic mixture is added over the FFA, and it is allowed to the esterification reaction to take place. Not all the details will be presented here.

52. If the saponification reaction is to take place, just move the FFA from vessel 9 to vessel 11 and add a strong mixture of KOH from vessel 4 and water from vessel 8. Allow the reaction to the procedure for a few hours and the final product will be liquid soap.

3. RESULTS AND DISCUSSION:

To execute the transesterification reaction 3 times ensures that the final product will achieve more than 99% of conversion from triglycerides to biodiesel. The removal of the crude glycerol in each transesterification step ensures the forward of the reaction with the use of smaller amounts of the catalytic mixture.

The reaction time was optimized with the use of an appropriate monitoring system. Monitoring of the transesterification reaction with real-time LASER spectroscopy allowed initiating the reaction at room temperature and increase the supply of energy (heat) throughout the reaction, reducing the energy consumption during the fuel production and the endpoint of chemical reaction of transesterification was detected by the monitoring system in the same way as it would do if the reaction was carried out under constant temperature. The endpoint is assumed when the reaction curve assumes a linear behavior, as in Figure 11.

The H_3PO_4 was chosen to acidify the crude glycerol due to the conversion of the catalyzer (KOH) into fertilizer (K_3PO_4). Other acids may be used as needed or to form other salts.

4. CONCLUSIONS:

The final main product, biodiesel, was obtained with the same characteristics as the one produced by traditional methods. The production costs were lower since the input of energy was smaller and the production time was shorter than traditional methods.

Performing the transesterification reactions near to the stoichiometric amounts reduced the refining time of the final product, as there were less unreacted raw, i.e., methanol, materials to be removed from the main product by flash destilation.

The ability to convert part of the byproducts (FFA) into biofuels or soaps allows the company to quickly change its production to serve the market sectors that offer greater profitability without compromising their productive capacity.

5. ACKNOWLEDGMENTS:

CAPES case: 9109/11-0

PETROBRAS/CNPq case: 142120/2009-0

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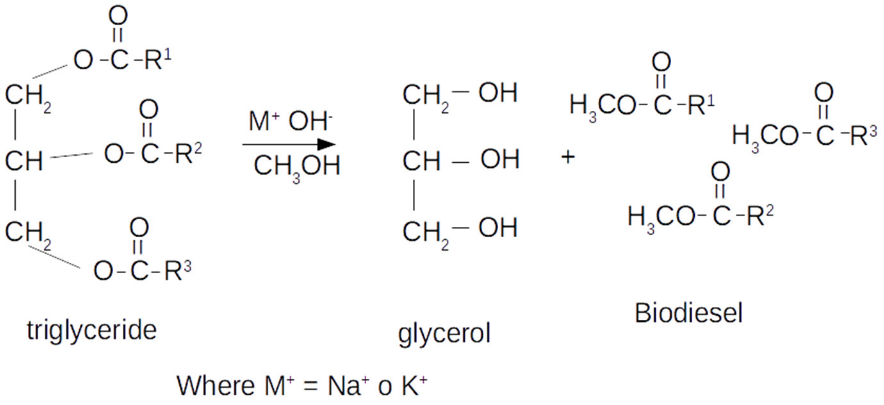


Figure 1: Transesterification: ester + alcohol → different alcohol + different ester

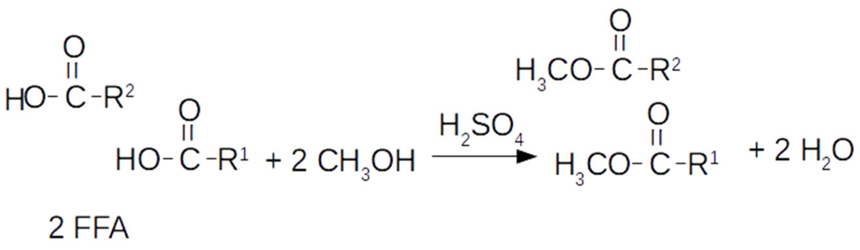
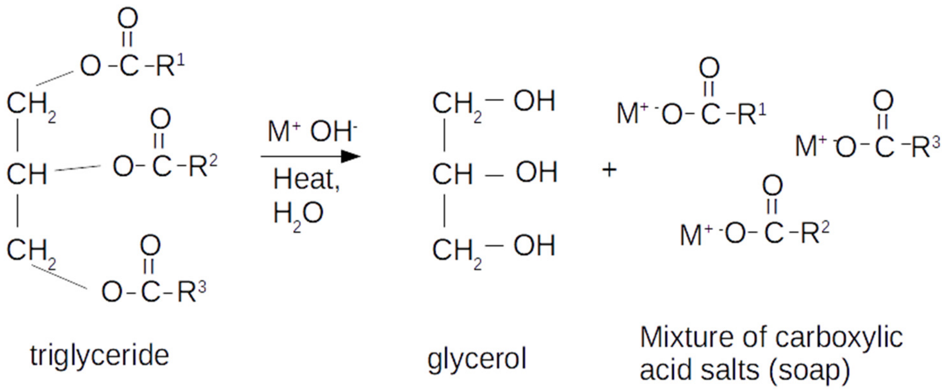


Figure 2: Esterification, free fatty acidy (FFA) + alcohol → ester + water



Where $M^+ = Na^+$ o K^+

Figure 3: Saponification: Triglyceride + Alkaline metal → glycerine + soap

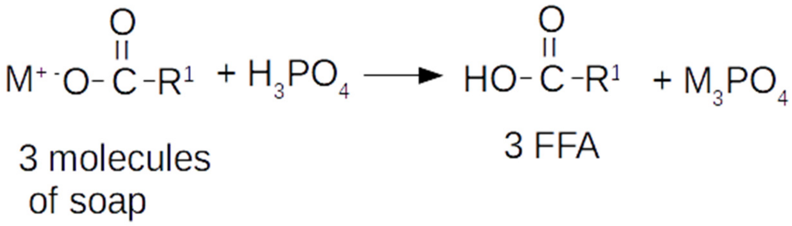


Figure 4: Acidification, soap + phosphoric acid → FFA + phosphoric acid salt.

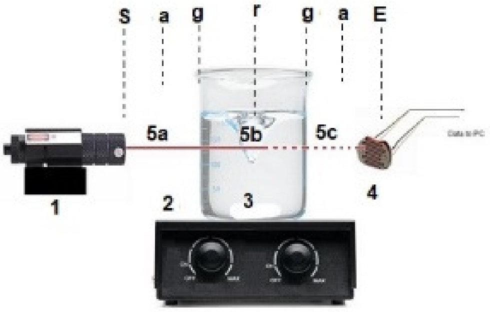


Figure 5: Schematic view of the setup of the reaction system monitored with real-time with LASER spectroscopy. Legend: 1- LASER source; 2- Heating plate; 3- Reactor; 4- Transducer; 5a- Incident LASER bean; 5b-Interaction between the LASER and the medium; 5c- output LASER radiation; S – propagation plane start point; E – propagation plane ending point; a – air environment; g – glass environment; r – reaction environment

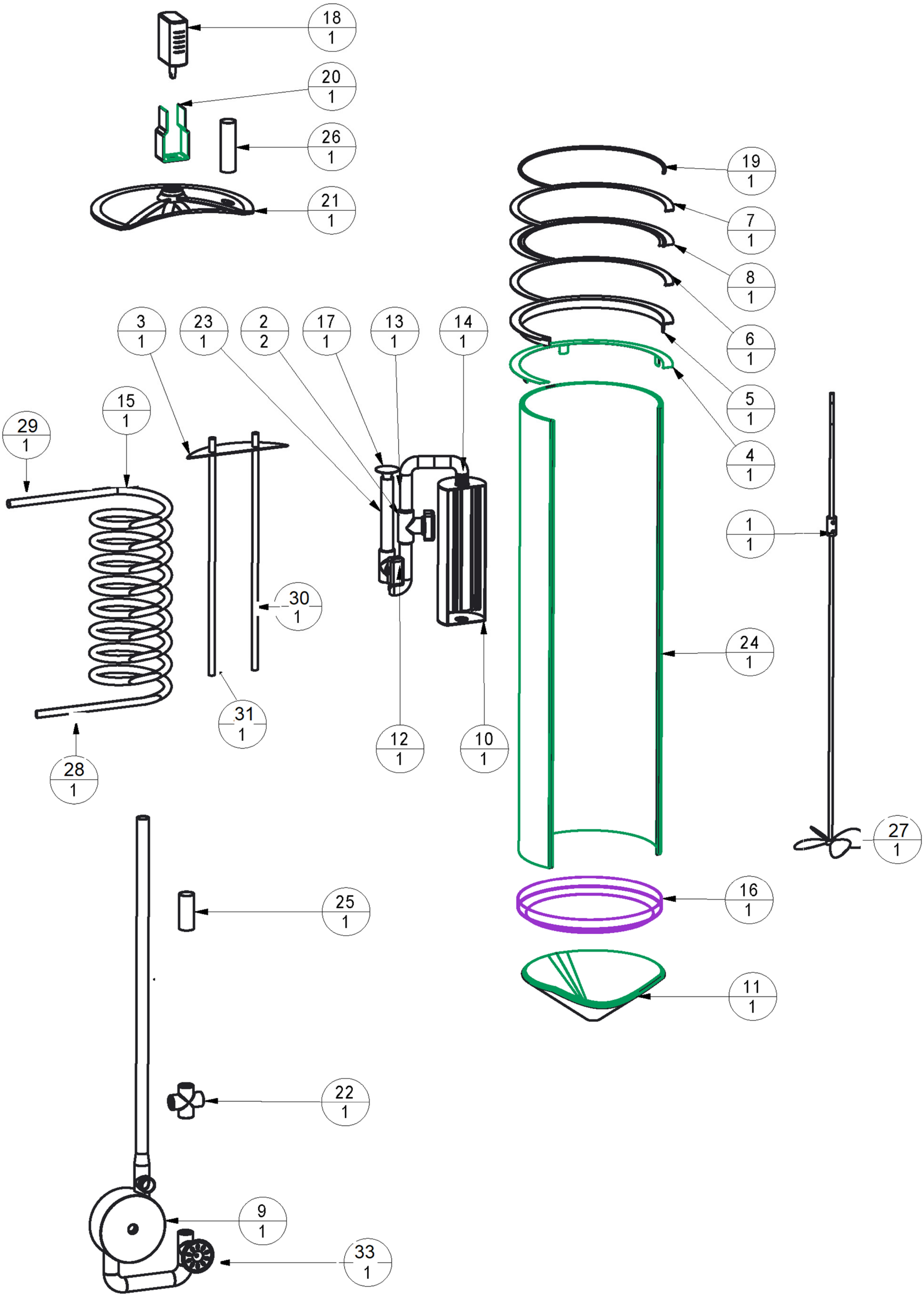


Figure 6: Reactor overview

Table 1: Reactor's components of Figure 6.

Number	Component	Amount
1	Shaft coupling	1
2	Actuator filter	2
3	Electrodes Bars	1
4	Upper flange base	1
5	External upper flange base	1
6	Inner upper flange base	1
7	External upper flange base	1
8	Upper flange base	1
9	Water pump	1
10	Housing filter	1
11	Bottom cone	1
12	90-degree bend fitting	1
13	Curve 90-degree filter input	1
14	90 Degree Curve Filter	1
15	Heating spiral	1
16	Tube seal - cone	1
17	Pressure Housing	1
18	Shaker motor	1
19	O-ring 304mm 5mm	1
20	Engine mount	1
21	Top cover structure	1
22	Exit cover	1
23	Wetting Tube	1
24	Main tube	1
25	Exit Tube 2	1
26	Vacuum tube	1
27	System shake propellers	1
28	Heating fluid outlet	1
29	Heating fluid inlet	1
30	Positive electrode	1
31	Negative electrode	1
32	Pipe	1
33	valve	

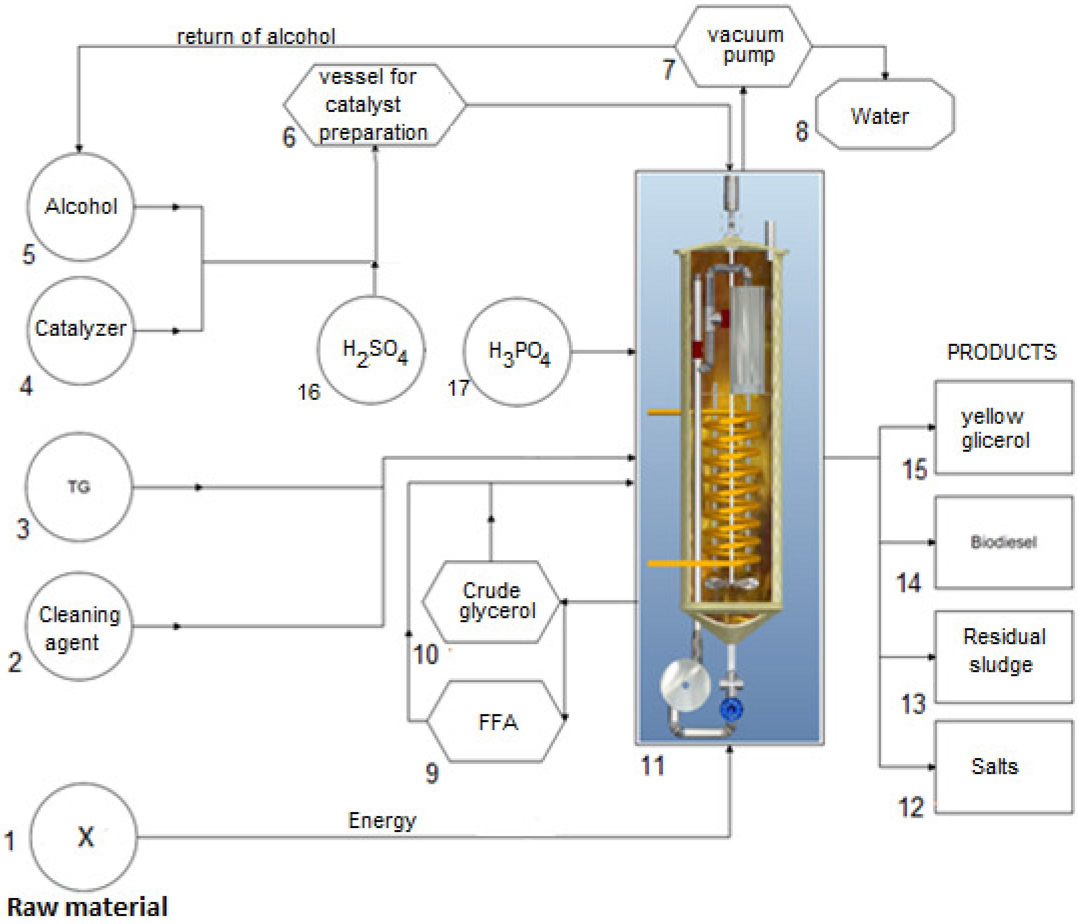


Figure 7: Generalized aspects of the system. Where: 1- Stock of wood or burning oil; 2- Stock of cleaning agent; 3- Stock of triglycerides (fat or oil); 4- Stock of catalyze ; 5- Stock of methanol; 6- tank for the preparation of the catalytic mixture ; 7- vacuum pump; 8- water storage tank; 9- FFA vessel; 10-Crude glycerol vessel ; 11- reactor; 12 – salt container; 13- residues; 14- biodiesel container; 15- yellow glycerin container.

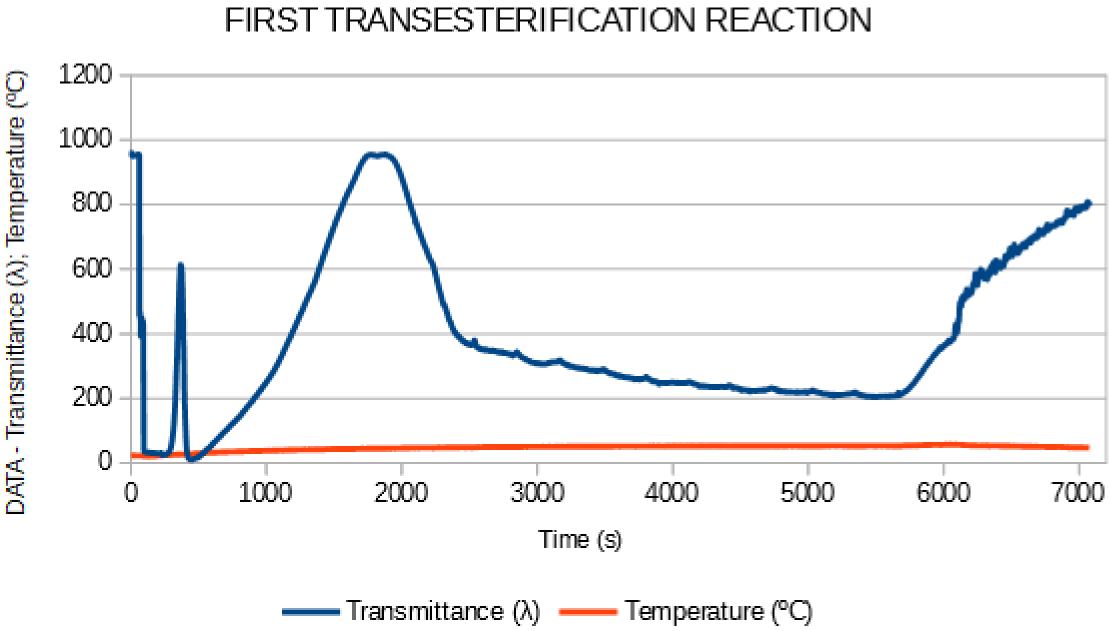


Figure 8 – First reaction of transesterification monitored with LASER spectroscopy and temperature monitoring.

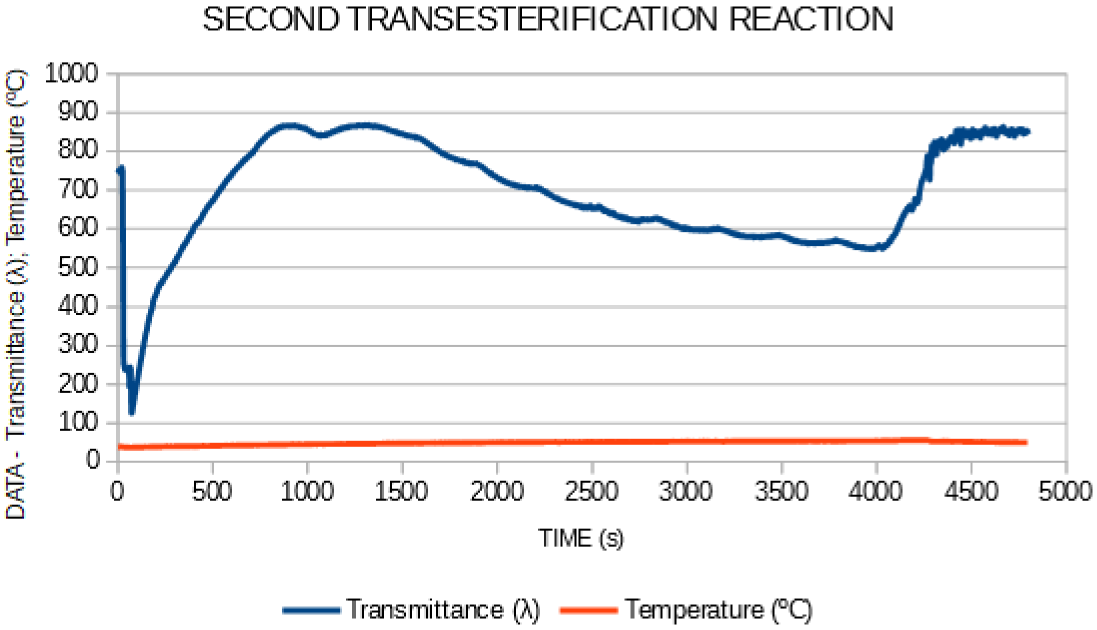


Figure 9 – Second reaction of transesterification monitored with LASER spectroscopy and temperature monitoring.

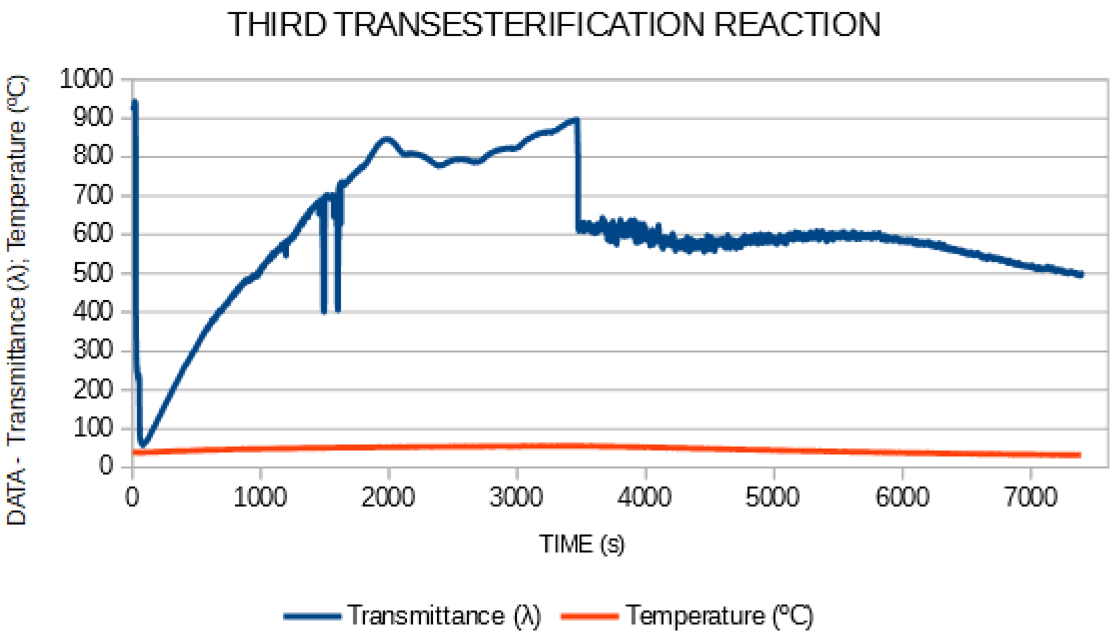
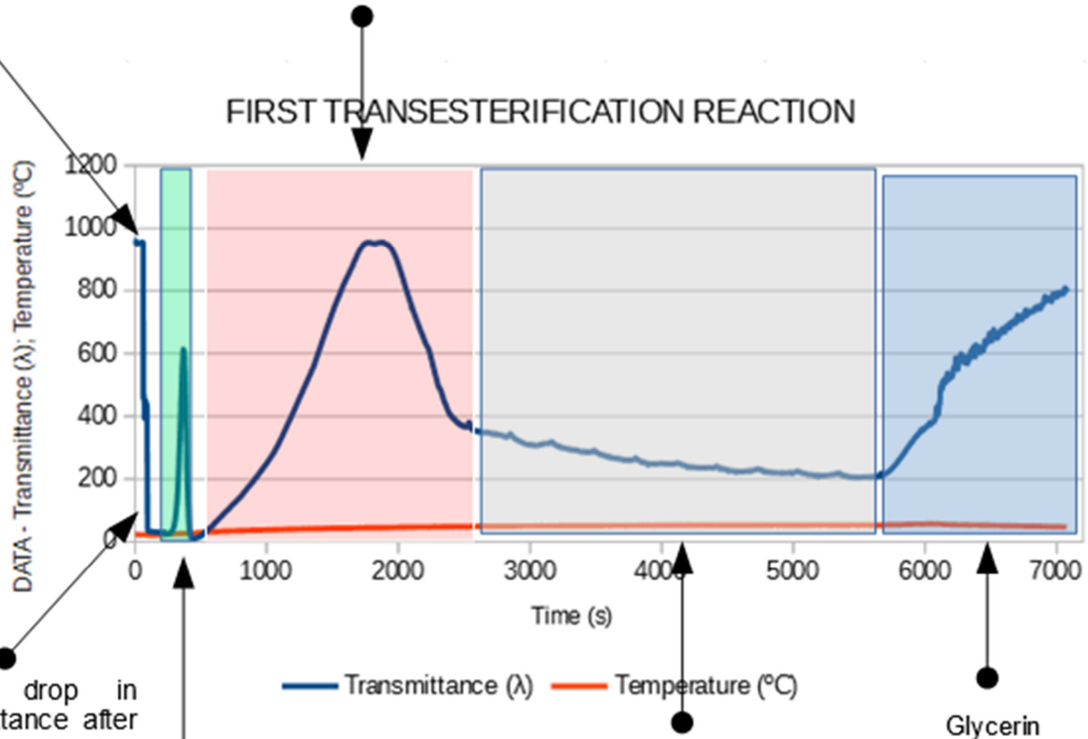


Figure 10: Third reaction of transesterification monitored with LASER spectroscopy and temperature monitoring. (In this graph the LASER was hit by the author's hand, and the distortion was caused by him fixing the sensor position. The glycerin separation was not monitored.)



Linear behavior before addition of the catalytic mixture.

Effective reaction time.

Strong drop in transmittance after addition of the catalytic mixture.

Moments of disturbance in the reaction, common just after the addition of the catalytic mixture. This peak may or may not appear depending on the position of the sensor within the reaction medium. This peak has no monitoring function or practical function and should be ignored when occurs, it is just an interference.

linear behavior of the instrumental reading, the reaction is in chemical balance. The reaction should have been interrupted much before 300s, but for demonstration purposes, it was allowed to proceed.

Glycerin separation phase

Figure 11: Comments on the monitoring process on the Graph.

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ARSENIC SPECIATION IN GROUNDWATER USING THE SOFTWARES PHREEQC, GWB AND GEODELING

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ABSTRACT

Geochemical modelling speciation is used to understand the interactions that occur in the groundwater. Thermodynamic data, kinetic parameters, numerical methods are factors that affect any geochemical modelling system. The conceptual formulation of geochemical modeling calculates the distribution of chemically reactive species for an aqueous solution. The mathematical formulation of the model results in a system of nonlinear algebraic equations that are solved using numerical methods. Most programs allow the user to estimate the speciation model. Activities of aqueous species are usually calculated using the Davies equation, Debye-Hückel equation, or the extended Debye-Hückel equation. We perform a comparative study of geochemical speciation using three different software: PHREEQC™, Geochemist's Workbench™ (GWB) and GEODELING. Details of each software take into account the distribution, mobility, and availability of chemical species in groundwater. We can observe very similar results in speciation when working with low-temperature systems (20 to 80°C). GWB™, PHREEQC™, and GEODELING employ an integrated system to define when to use Davies, Debye-Huckel or B-dot equation, according to the value of the solution ionic strength. The geochemical speciation aimed to compare the results of simulators able to predict the chemical species present in groundwater. The utilization of GEODELING allows comparing the results with software GWB™ and PHREEQC™ with a high degree of acceptance for low temperatures. The numerical methods used by GWB™, PHREEQC™, and GEODELING software are able to seek its own best set of numerical solutions to achieve the equilibrium. Users must be cautious when choosing geochemical modeling software, as an essential factor for choosing a simulator is to know the temperature range that will be used.

Keywords: *Hydrogeochemistry, Carcinogenic Metalloid, Arsenic Prediction Model, Geostatistical, Reactive Transport.*

1. INTRODUCTION

Arsenic (As) and its compounds are present in nature and exhibit both metallic and nonmetallic character in their properties. The trivalent (3+) and pentavalent (5+) forms are the most common oxidation states (Arsic *et al.,* 2018). From a toxicological point of view, the arsenic compounds can be classified into three groups: inorganic arsenic compounds; organic arsenic compounds; and arsine gas. Inorganic compounds with 3+ valency are arsenic trioxide, sodium arsenite, and arsenic trichloride. In turn, compounds with valency 5+ are arsenic pentoxide, arsenic acid and arsenates (lead arsenate and calcium arsenate) (Bennett *et al.,* 2012). Common organic arsenic compounds are arsanilic acid, methylarsonic acid, dimethylarsinic acid (cacodylic acid) and arsenobetaine (Yu *et al.,* 2018).

Arsenic trioxide is only slightly soluble in water; in sodium hydroxide forms arsenite and with concentrated hydrochloric acid in the form of arsenic trichloride. Sodium arsenite and sodium arsenate are high soluble in water. Interchanges of valence state may occur in aqueous solutions, depending on the pH and on the presence of other substances which can be reduced or oxidized

(Correia *et al.,* 2010). Arsenic appears in nature mainly in the form of sulfides associated with silver ores, lead, copper, nickel, antimony, cobalt, and iron (Lock *et al.,* 2018).

Trace amounts of arsenic are found in soils and other geological environments. Arsenic is mainly transported into the environment by water. In aqueous environment arsenic usually occurs as arsenate (AsO_4^{3-}), but under reducing conditions, for example, in deep waters, the arsenite (AsO_3^{3-}) species predominates (Wang *et at.,* 2015).

In oxygenated soil, inorganic arsenic is present in the pentavalent form. Under reducing conditions, it is in the trivalent form (Lock *et al.,* 2016a). Arsenic is released to the atmosphere from both natural and anthropogenic sources. The principal natural source is volcanic activity, with minor contributions by exudates from vegetation and windblown dust. Man-made emissions to air arise from the smelting of metals, the combustion of fuels, especially of low-grade brown coal, and the use of pesticides (Lock *et al.,* 2016b).

2. HYDROGEOCHEMISTRY OF ARSENIC

The models that can describe and predict the transport of arsenic into groundwater are very relevant to determine the extent of arsenic contamination and to evaluate alternatives for groundwater remediation. Such models should incorporate the various factors that affect the transport of arsenic into groundwater. The most common mineral with associated arsenic is arsenopyrite (FeAsS) (O'Neill, 1995; Pokrovski *et al.,* 2002, Webster, 1999), common in several mineral deposits with sulfides (Savage et al., 2000). The oxidation of pyrite due to mining can cause acid drainage (Evangelou and Zhang, 1995), potentially mobilizing associated arsenic. The distribution of arsenic in sediments and soils is often controlled by the characteristics of the underlying rocks (Wang *et at.,* 2015). Inorganic arsenic is mainly present as As(5+), forming arsenic acid ($H_2AsO_4^-$ and $HAsO_4^{2-}$) species, while in the reducing waters As(3+) is thermodynamically stable, forming the arsenous acid (H_3AsO_3) (Arsic *et al.,* 2018).

The geochemical mobility of arsenic in groundwater can be significantly delayed or increased due to reactions that occur in the water-rock interaction (Sun *et al.,* 2016). The properties of mineral surfaces and their interactions with arsenic are essential in determining the fate and transport of arsenic in groundwater. In general, physico-chemical processes such as precipitation, dissolution, complexation and ion exchange may have the properties of the element affecting its availability in the geological environment (Wu *et al.,* 2017). This work aims to compare the speciation models generated by the GWB™, PHREEQC™ and GEODELING software of four sampling points underground water in arsenic concentrations. This study also allows us to validate the results of the commercial software (GWB™ and PHREEQC™) with its own code (GEODELING).

3. CONCEPTUAL MODEL

3.1. Process simulation

The fate of arsenic does not depend only on physical processes of transport, also depending on geochemical reactions. Arsenic is a trace element whose speciation in groundwater is controlled by pH (hydrogen ions activity) and pE (electron activity - redox potential) (Wang *et at.,* 2015).

3.2. Initial conditions of the water speciation

A numerical simulation study, predicting the geochemical speciation of arsenic in groundwater, was carried out with GWB™ and PHREEQC™ software with the aim of comparing the results obtained with GEODELING code. The temperatures used for simulations are 20, 40, 60 and 80 °C Table 1. The experimental temperatures were set according to klunk *et al.,* 2015.

Table 1: Chemical composition of the arsenic in groundwater (x10^{-3} g/L).

Element	AS1	AS2	AS3	AS4
As	8.19	7.44	5.67	4.82
pH	4.71	5.15	5.80	5.92
pE	9.03	8.72	8.55	8.43

The initial conditions of simulation using the GEODELING have as its starting point the combination of the chemical species. The new concentrations are calculated and represented by the logarithm activity of ionic species. The activity concentration is used to eliminate the effect of the interaction between the ions in solution. The partial pressure of CO_2 solution was 2.0 MPa (at pH value of about 5.0). The pressures were set as the hydrostatic pressure at about the depths corresponding to the strata temperatures (slightly adjusted). Was carry out four sampling point (AS1, AS2, AS3, and AS4) in groundwater.

3.3. Softwares de modelagem Geoquímica

GEODELING was developed from the thermodynamic model based on the numerical method of $\text{DISSOL}^{\text{TM}}$ (Fritz, 1975, 1981). This thermodynamic code was expanded through the introduction of kinetic laws governing the geochemical speciation (Helgeson and James 1968) in order to make numerical simulations possible in time functions (Lasaga et al., 1994). Thus, in the thermodynamic and kinetic model of the code GEODELING, the mineral reaction rates are controlled by the molecular diffusion of the aqueous phase and a porous layer formed by the dissolution or precipitation of a mineral. The own speciation code has application in the physical, chemical aqueous and geochemical useful tool with the intuitive and interactive interface.

Geochemist's $\text{Workbench}^{\text{TM}}$ (GWB^{TM}) was developed by the Department of Geology at the University of Illinois at Urbana-Champaign in 1978 (Bethke 2008). GWB^{TM} use modules SpecE8 and GSS in “React Mode” for speciation model. The user sets the initial condition (concentration of species) of the geochemical system in thermodynamic equilibrium. So, the GWB^{TM} start the calculation and necessary interactions that lead to speciation model. When GWB^{TM} finished the simulation, output data is generated.

$\text{PHREEQC}^{\text{TM}}$ is software written in programming languages C and C++ designed to perform a wide range of geochemical calculations (Parkhurst and Appelo, 1999). $\text{PHREEQC}^{\text{TM}}$ is capable to (1) calculate the saturation index and speciation, (2) calculate the reactions in "batch model" and transport one-dimensional (1D), (3) use the Pitzer model for high salinity water that is an outside range of application of the Debye-Huckel theory (Pitzer, 1991). The software uses a numerical method of integration allowing solution of ordinary differential equations, which can be generalized for the reconstruction of three-dimensional trajectories (Parkhurst and Plummer 1993).

4. RESULTS AND DISCUSSION

Events predicted by numeric simulation between 20 and 80°C using GWB^{TM}, $\text{PHREEQC}^{\text{TM,}}$ and GEODELING, are summarized in Figure 1.

GEODELING code was built to predict the species present in groundwater. The various simulations in this study enabled a comparative study of GEODELING behavior with commercial software speciation (Fig. 1). The results showed that the use of different codes produces little different results during modeling low temperature (20 to 80°C). Generally, the simulation results show the same behavior, because each software uses similar numerical methods to solve a different set of reactions.

Each simulator has its algorithms based on numeric methods that are dependent on kinetic and thermodynamic parameters, contained in the database. Users must be careful when choosing a geochemical speciation software because, depending on the temperature range, different systems can produce very discrepant behaviors. GWB^{TM}, $\text{PHREEQC}^{\text{TM,}}$ and GEODELING using a similar numerical method in this temperature range, the plotted profiles appear practically the same.

5. CONCLUSIONS

The present study of geochemical speciation compare the application of GWB^{TM}, and $\text{PHREEQC}^{\text{TM}}$ codes with GEODELING for the simulation of groundwater resulting in the follow conclusions:

1) Reactions at low temperatures (20 to 80°C) with different simulators reproduce quite the same behaviors. In this temperature range, which involves low energy, the reaction kinetics, and the thermodynamic parameters behave according to the particularities of each code. The numerical methods used by GWB^{TM}, $\text{PHREEQC}^{\text{TM}}$ and GEODELING software can achieve only limited convergence of results, with the high precision expected for reactions at low-temperature geological environments.

2) The geochemical speciation aimed to compare the results of simulators able to predict the chemical species present in groundwater. The utilization of GEODELING allows comparing the results with software GWB^{TM} and $\text{PHREEQC}^{\text{TM}}$ with a high degree of acceptance for low temperatures.

3) The numerical methods used by GWB^{TM}, $\text{PHREEQC}^{\text{TM,}}$ and GEODELING software are able to seek its own best set of numerical solutions to achieve the equilibrium.

Users must be cautious when choosing geochemical modeling software, as an essential factor for choosing a simulator is to know the temperature range that will be used.

6. ACKNOWLEDGMENTS

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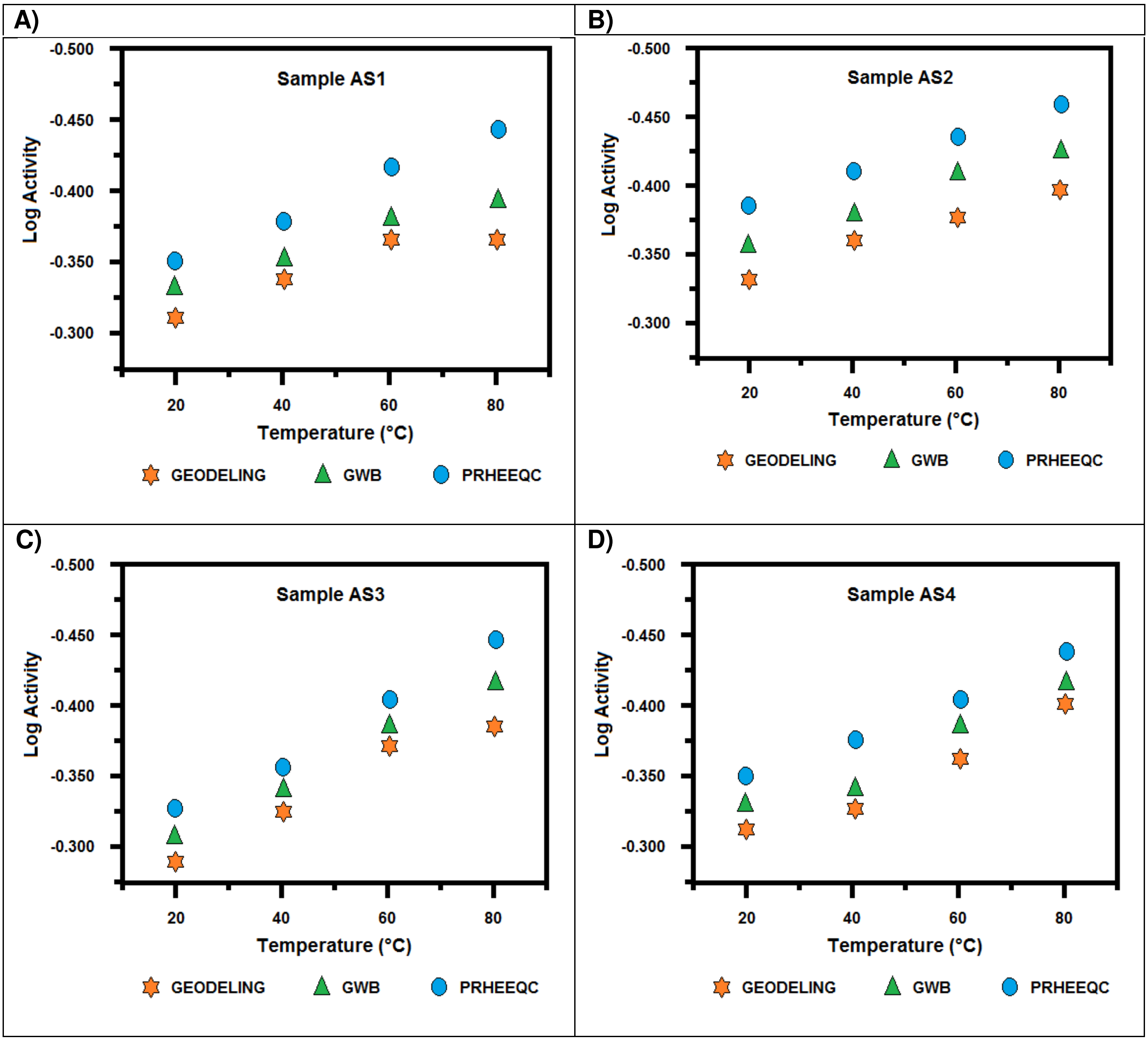

Figure 1. *Speciation model using GEODELING, GWB^{TM} and PHREEQC^{TM}.*

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