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SYSTEM OF ADSORPTION OF CO_2 IN COALBED

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ABSTRACT

Carbon capture and storage (CCS) has been observed as an alternative measure to mitigate emissions from greenhouse gases. CCS systems separate CO_2 during the process of converting fuel and transport to the facilities where they are stored, e.g., under geological formation conditions. Capture and sequestration technologies are now widely used in different industries. CO_2 capture is currently a costly and energy-consuming technology. The costs obviously depend on the size of the plant and the type of fuel used. Generally, capture systems are categorized into three categories: pre-combustion, post-combustion, and oxy-fuel combustion. The saline aquifer, depleted oil, and gas fields are large-capacity storage sinks. The coalbeds also provide as a substitute to geological storage. One of the main advantages of coal storage is renewable methane fuel and coal desulfurization. The studied coal reserves are located in Candiota, State of Rio Grande do Sul, Brazil. These are the largest coal deposits in the country, with a reserve of 1 billion tons. This work will represent a study on CO_2 storage in Candiota coalbed system. The use of a synthetic CO_2 cylinder with a flow of 0.2 L /min varies the time of contact with the coalbed. The results from the volatile matter increase by 11%. The results of the ultimate analysis exhibited an 8% increase for carbon and oxygen after 60 minutes of CO_2 flow in the coalbed. On the other hand, there was a reduction of 32% for sulfur. The resultant phenomena occur due to the adsorption capacity of CO_2, where the compounds are released from the pores of coal.

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METHODOLOGY FOR DETERMINATION OF DEGREE OF NODULARITY IN A DUCTILE CAST IRON GGG 40 BY ULTRASONIC VELOCITY TEST

AGNOLETTO, Douglas [1, *]; LEMOS, Guilherme Vieira Braga[1, 2]; BESKOW, Arthur Bortolini [1]; LESSA, Cleber Rodrigo de Lima[3]; REGULY, Afonso[2]

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ABSTRACT

Cast iron alloys combine many elements such as carbon, iron, silicon, magnesium and can be usually classified according to their microstructure in ductile, gray, compacted, white, and malleable. Each one has particularities in terms of properties and applications. Hence, this study aims to evaluate the degree of nodularity (%) in a ductile cast iron alloy GGG 40. In this context, a methodology to investigate the degree of nodularity was proposed. The ultrasonic method was used to determine the amount of ductile graphite as well as for parts release and thus facilitated the industrial operational execution. The effect of ultrasonic sound was investigated in sixty-seven ductile cast irons, and these analyses were further compared to the level of nodularity observed by metallography. Finally, based on the findings, the cast iron quality was guaranteed, leading to time-savings, avoiding the microstructural examination, and thus promoting cost reductions.

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SLOW PYROLYSIS OF RICE STRAW: ANALYSIS OF BIOCHAR, BIO-OIL AND GAS

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ABSTRACT

Biomass is the term attributed to any renewable resource derived from organic matter that can be used in energy production. Agricultural production generates residues that are of great importance for their energy use, of which sugar cane, eucalyptus, and rice. Various residues are generated from rice cultivation, among which the rice husk and rice straw are the most important. Several thermal conversion technologies have been developed for the use of biomass in industry. Pyrolysis has been notable for its ability to produce biofuels at different stages of aggregation. The slow pyrolysis of biomass has been proposed as a pretreatment method to improve the physical-chemical characteristics of rice straw. In this process is produced, mainly, a solid called biochar, which has a higher energy content when compared to the biomass of origin. This study investigated the slow pyrolysis of rice straw at 300 - 700°C for the purpose of obtaining biochar, bio-oil, and gases for energy purposes. The experimental results show that pyrolysis temperature has important roles in yield product. The highest biochar yield was observed at a temperature of 300°C with 49.91 wt%. This represents 47% more when compared to yield at 700°C (33.87 wt.%). This behavior is linked to the proximate analysis results for fixed carbon 26.01 wt.% at 300°C. The high pH of the biochar was attributed to the presence of alkali metals, according to XRF. Thermal decomposition of the biomass resulting in a gradual increase of bio-oil (16.81 - 34.70 wt.%) and gas (6.53 - 18.05 wt.%) on a wet basis. Thus, in the dry base parameter, the bio-oil increases from 19.22 - 30.6 wt.% and the gases at 9.42-20.19 wt.%. Drying of the raw material showed, by the results, a significant increase in the co-products formed. As a consequence, we have a more efficient energy process.

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STUDY OF ALAZANI RIVER AND SURFACE WATER COMPOSITION IN SOME VILLAGES OF KAKHETI REGION OF GEORGIA

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ABSTRACT

The article reviews the chemical composition of borehole and surface waters in three villages of one of the regions of Georgia - Kakheti, Gurjaani Municipality. The study was specifically focused on iodine content in waters. It turned out that certain amount of iodine really existed in borehole waters, which means that by everyday drinking of water, the human body gets maybe not the complete required amount of iodine, but at least some part of it. It was also discovered, that according to certain parameters, waters are clean, do not contain heavy metals and can be freely used for drinking and cooking. The chemical composition of the Alazani River was also examined according to all four seasons. This river is interesting because of being used for irrigation of vineyards and fruit gardens.

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WASTE FRYING OIL TRANSESTERIFICATION TREATED BY STEAM DRAG METHOD

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ABSTRACT

Demand for diversified biodiesel feedstocks is high and increasing, but few are viable for large-scale production, and many of those selected compete with other sectors of the chemical industry. To improve energy and environmental sustainability, fatty acids from waste oils that are improperly disposed of and pollute the environment can be used for transesterification reactions. However, they need treatment to achieve high conversion rates. In this context, the aim of this work was to perform and analyze the treatment of residual frying oil with the evaporation and entrainment process, aiming at its use as raw material to obtain biodiesel (methyl esters) by a transesterification reaction. The physicochemical properties of the residual oil after treatment were characterized by moisture content, pH and the acidity, saponification, iodine, and peroxide index. The conversion rate of the residual oil to methyl esters was determined by 1H NMR analysis. After the treatment, the method of analysis of variance showed that the oil obtained a significant reduction of the saponification, iodine, peroxide and acidity indexes, being the acidity reduced from 9.36 to 7.85 mg KOH g-1. The moisture content of 0.733 % and elevation of pH to 8.0. The conversion rate of fatty acid biodiesel of residual oil was 79.3 %, lower value of standards norms (ASTM, 2005; EN, 2008; ANP, 2014), showing that the assigned methodology for frying residual oil is inefficient in biodiesel production.

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TO AUTHORS

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SYSTEM OF ADSORPTION OF CO_2 IN COALBED

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ABSTRACT

Carbon capture and storage (CCS) has been observed as an alternative measure to mitigate emissions from greenhouse gases. CCS systems separate CO_2 during the process of converting fuel and transport to the facilities where they are stored, e.g., under geological formation conditions. Capture and sequestration technologies are now widely used in different industries. CO_2 capture is currently a costly and energy-consuming technology. The costs obviously depend on the size of the plant and the type of fuel used. Generally, capture systems are categorized into three categories: pre-combustion, post-combustion, and oxy-fuel combustion. The saline aquifer, depleted oil, and gas fields are large-capacity storage sinks. The coalbeds also provide as a substitute to geological storage. One of the main advantages of coal storage is renewable methane fuel and coal desulfurization. The studied coal reserves are located in Candiota, State of Rio Grande do Sul, Brazil. These are the largest coal deposits in the country, with a reserve of 1 billion tons. This work will represent a study on CO_2 storage in Candiota coalbed system. The use of a synthetic CO_2 cylinder with a flow of 0.2 L /min varies the time of contact with the coalbed. The results from the volatile matter increase by 11%. The results of the ultimate analysis exhibited an 8% increase for carbon and oxygen after 60 minutes of CO_2 flow in the coalbed. On the other hand, there was a reduction of 32% for sulfur. The resultant phenomena occur due to the adsorption capacity of CO_2, where the compounds are released from the pores of coal.

Keywords: *Greenhouse Gases, Climate Change, Candiota Coalfield, Carbon Capture, and Storage.*

1. INTRODUCTION

The burning of fossil fuels emits a substantial amount of greenhouse gases (GHG), where carbon dioxide (CO_2) is most abundant (Chen *et al.,* 2017). The emission of this gas into the atmosphere causes the natural phenomenon of heat retention on Earth's surface to be aggravated, causing climatic changes (Fernández-Sánchez *et al.,* 2015). These changes in climate, in turn, activate a set of changes related to the operation of ecosystems (Kim and Kim, 2016; IPCC, 2014). As a procedure of mitigating environmental impacts, the geological, oceanic and biological storage of CO_2 are technological alternatives that have been discovered. Geological storage is the process which follows the capture and transport of CO_2 (Man *et al.,* 2018).

Capture and transport take place from the source to reservoirs which are capable of retaining CO_2 for hundreds or thousands of years. This technology system is called Carbon Capture and Storage (CCS). Carbon capture and storage systems occur with separation of CO_2 during the process of energetic conversion of fossil fuel to different geological formations (IPCC, 2014). The reservoirs currently used are depleted oil and gas fields, saline aquifers and Carboniferous formations (Agartan *et al.,* 2018; Hosa *et al.,* 2011; Qi *et al.,* 2009; Hassanzadeh *et al.,* 2008). The use of carboniferous formations as a reservoir occurs when the coal is no longer operable and the extraction of methane (CH_4) adsorbed in the pores of the geological formation and desulfurization of the coal with high SO_2 contents due to the presence of pyrite is desired (Shogenov *et al.,* 2017; Xia and Xie, 2017; Borah and Baruah, 2001).

In order to achieve the storage of large volumes of CO_2, the geological formation requires to have adequate permeability (Jiskani *et al.,*

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2018; Marcisz *et al.,* 2018). The logistics of CO_2 capture, transport, and storage are not trivial, and risks of leakage are involved at all stages (Deng *et al.,* 2014; Keller *et al.,* 2008). The characteristics of the reservoir and possible escape mechanisms of CO_2 must be carefully monitored to avoid catastrophe in the environment (Deng *et al.,* 2014).

This particular work aims to study a CO_2 adsorption system in coalbed in order to properly capture and store CO_2 in order to sustain for a long inactive period of time. The coals of Candiota, State of Rio Grande do Sul, Brazil, were utilized for this purpose. In a system simulating coalbeds, CO_2 could be stored. This is evident in the results of proximate and ultimate analyses where there was an increase of 11% in the volatile matter and a decrease of 32% in sulfur contents.

2. CO_2 CAPTURE, TRANSPORTATION AND STORAGE TECHNOLOGIES

Carbon is an essential chemical element of life. It occurs in nature as graphite and/or diamond, it is also associated with other atoms such as carbon dioxide, coal, methane, etc. (Reiter and Lindorfer, 2015). The development of modern society is based on activities which provoke an increase in carbon. In this context, we can mention: soil use (agriculture, forest burning); ii) industrial activities (petrochemical); iii) the burning of fossil fuels (coal, oil and natural gas) for generating power (Koytsoumpa *et al.,* 2018).

As there are no natural mechanisms to convert carbon at the same rate as it is transferred, CO_2 ends up concentrating on the atmosphere. This increase in CO_2 concentration causes the greenhouse effect in the atmosphere (Huaman and Lourenco, 2015). Other gases are also responsible for this disastrous effect on the atmosphere, which includes nitrous oxide (N_2O), methane (CH_4) and chlorofluorocarbons (CFC's). Among GHGs, CO_2 possesses the maximum concentration (approximately 75%) in the atmosphere (Deng *et al.,* 2014).

2.1. CO_2 capture

Generally, capture systems are classified into three categories: pre-combustion, post-combustion, and oxyfuel combustion.

2.1.1. Pre-combustion capture

The technology for pre-combustion is extensively applied for chemical, gaseous fuel (H_2 and CH_4), fertilizer, and also for power production (Mantripragada and Rubin, 2017). In these particular cases, the fossil fuel is partially oxidized in a gasifier. CO from the derived syngas (CO and H_2) reacts with additional steam (H_2O) and is thereby converted into CO_2 and H_2 (Zheng *et al.,* 2017). The resultant CO_2 can be captured from a comparatively pure exhaust stream. H_2 can further be used as fuel, whereas, removal of CO_2 takes place before combustion. There are various advantages and disadvantages when this method is compared to conventional post-combustion carbon dioxide capture (Kanniche *et al.,* 2010). In this method, CO_2 is removed after combustion of fossil fuels, but before the expansion of flue gas in the atmospheric pressure. This method is applied to contemporary fossil fuel burning power plants, or to existing plants where re-powering is an alternative (Park *et al.,* 2015). The capture which occurs before expansion, i.e., from pressurized gas, is the standard in almost all the industrial CO_2 capture processes at the same scale as required for utility power plants.

Pre-combustion capture also has the advantage of excessive control of CO_2 emissions (90 to 95% of CO_2 is captured). It involves low technological risk and also has the possibility of becoming the most efficient method to mitigate CO_2 emissions (Ryu *et al.,* 2017).

2.1.2. Post-combustion capture

Post-combustion systems retain CO_2 capture after the burning of fossil fuel (Wu *et al.,* 2014). In this case, CO_2 is captured from flue gases at several power stations or other massive point sources. The technology is well comprehended and is presently used in distinct industrial applications, although at a different scale than required in a commercial scale power station (Moser *et al.,* 2013). Post-combustion capture is most accepted for research purpose since the existing fossil fuel power plants can be retrofitted for including CCS technology in this specific configuration (Singh, 2013). There are several methods which can be applied to capture CO_2 in post-combustion processes (Jin *et al.,* 2018). One significant method is the separation of the gases produced and emitted into the atmosphere through the absorption process (Plaza *et al.,* 2017). This includes a mass transfer between the gas (combustion gas) and liquid (solvent) phases, which exploits the differences in the gas-liquid solubility of distinct components of the treated mixture. Another post-combustion capture process is adsorption, which involves utilization of a solid surface, such as activated carbon or zeolites to adsorb CO_2 present in a particular gas mixture (Moser *et al.,* 2013. Separation of CO_2 by membranes is another significant process associated with capture. The membranes cannot separate the CO_2 with the required efficiency in only one step. It is, therefore, necessary to repeat the process until a suitable degree of purity has been achieved. This is responsible for increasing the complexity associated with increasing energy consumption and costs in the system (Jin *et al.,* 2018).

2.1.3. Oxy-fuel combustion

In oxy-fuel combustion method, the fuel is burned in oxygen instead of air (Dwivedi *et al.,* 2018). The cooled flue gas is re-circulated and then injected into the combustion chamber to limit the resultant flame temperature up to the levels of conventional combustion (Hu *et al.,* 2018). The flue gas consists of mainly carbon dioxide and water vapor, where the latter is condensed through cooling (Leffler *et al.,* 2017). The outcome of the process is an almost pure carbon dioxide stream, which can be conveyed to the sequestration site and stored. Power plant processes associated with oxy-fuel combustion are frequently referred to as "zero emission" cycles. In these processes, the preserved CO_2 does not occur as a fraction removed from the flue gas stream (like in pre- and post-combustion capture methods), but the overall flue gas stream itself (Carrasco-Maldonado *et al.,* 2017). A certain fraction of the generated CO_2 during combustion will inevitably end up as a constituent of the condensed water. The water has to be treated or disposed of appropriately for authorization of the “zero emission” label. The oxy-fuel combustion technique is promising, but the initial step of air separation requires a lot of energy (Chen, 2018).

2.2. CO_2 transport

CO_2 transport is the least complicated process in the CCS chain, as it is an existing technology for which relevant costs can be estimated (Goldthorpe and Ahmad, 2017). The principal complication with CO_2 transport is that this compound behaves in different ways when subjected to variations in pressure and temperature (Jakobsen *et al.,* 2017). Thus, the transfer of CO_2 has to be carefully managed to prevent solidification and occurrence of blockages. There are two effective methods for transporting massive volumes of CO_2: pipeline transport and ship transport. Transportation is also possible through trucks with CO_2, usually in liquid form. However, these two solutions are not feasible for substantial quantities (Engel and Kathe, 2017).

2.3. CO_2 storage

In several places of the world, CO_2 is trapped in carboniferous formations (He *et al.,* 2011). The idea of geological storage further seeks to reproduce such natural phenomenon which attests to the great potential that geological formations have for storage of gases (Shogenov *et al.,* 2017).

Several aspects need to be considered when it comes to CO_2 storage: (i) the storage period should be extensive, preferably hundreds or thousands of years; (ii) the cost of storage, including transport from the place of capture, injection, and monitoring, should be minimized; (iii) the applied methods may not violate any national or international law or regulation; (iv) the environmental impacts need to be carefully considered, and their minimization techniques should be assessed; (v) the probability of occurrence of accidents should be practically null (Zhao *et al.,* 2016). Coal is the sedimentary rock which results from the decomposition of organic matter and is generally found in veins or layers (Maphala and Wagner, 2012).

If CO_2 is injected into coal deposits, CO_2 will release the trapped CH_4 therein and fill the voids where it was located. Based on laboratory studies, it is estimated that a volume of CO_2 can be stored twice as large as that of CH_4 initially adsorbed (Chai and Shimada, 2011). Since this technique leads to an improvement in the yield of a deposit in terms of collected natural gas, it became popular as Enhanced Coalbed Methane Recovery (ECBMR) (Fan *et al.,* 2018). ECBMR is a more efficient method for capturing more than 90% gas than the traditional methods for CH_4 collection from coal which captures about 50% of the gas (Vishal *et al.,* 2018; Ma *et al.,* 2017).

3.2. MATERIALS AND METHODS

3.1. Coal geology

Coal is a biogenic sedimentary rock, which is easily combustible and is brown to black in color. It is derived from the decomposition of accumulated debris in a basin from the atmosphere, on which sediments were deposited (Wang *et al.,* 2018). The formation consisting of the coal goes through an initial phase of slow biodegradation of the accumulated material by anaerobic microorganisms (Fuertez *et al.,* 2017). Both biochemical and thermodynamic processes occur with the successive deposition of inert gases on this organic sludge (Davis and Gerlach, 2018). Dehydration is accompanied by impoverishment in the volatile matter, along with loss of oxygen and hydrogen. The resulting mass, enriched in carbon, decreases in volume, and increases in density due to the combined action of pressure and temperature (Wang *et al.,* 2018).

The constituents of coal which can be distinguished microscopically are called macerals. The term "maceral" is analogous to the use of the term mineral while speaking of igneous or metamorphic rocks. However, unlike minerals, macerals have no characteristic crystalline form and are not constant in their chemical composition and physical properties. One of the most common macerals is vitrinite, which is derived from woody materials (Zieger *et al.,* 2018). Vitrinite is considered to be the most important maceral due to its extraordinary adsorption power of CO_2, causing a greater increase of volume of the same and, consequently reducing the permeability of coal (Zieger *et al.,* 2018).

The proportion in which the different macerals present themselves, as well as the level of their maturation, have consequences on the chemical, physical, and mechanical properties of the coal. Therefore, there occurred a requirement to classify the various types of coal. One of the most widely used concepts is the rank of coal. This is an important feature as it is widely used by coal-burning industries to infer the calorific value of the fuel (Fuertez *et al.,* 2017).

The degree of coal is estimated by a specific energy, evaluation of the water content, percentage of volatile matter or reflectance of vitrinite. A single parameter is not sufficient to classify the different grades of coal, and however, sometimes more parameters are used for one rank than others. The low-rank coals are generally characterized by the heat energy value and the water content, whereas the high-rank coals are distinguished using the reflectance values of vitrinite, the presence of fixed carbon and the percentages of volatile matter (Zieger *et al.,* 2018).

3.2. Location of the study area

The study area is located in the city of Candiota, at the southern end of the State of Rio Grande do Sul, Brazil. The Presidente Médici thermoelectric power plant belongs to Eletrobrás - Companhia de Geração Térmica de Energia Elétrica SA (CGTEE) and is provided by Companhia Riograndense de Mineração (CRM), which has reserves of $1{,}419.41 \times 10^6$ tons (CRM, 2010) and a production of 1,600,000 tons per year of ore to meet the needs of the plant.

3.3. Preparation of coal samples and CO_2 injection system

The coal samples were inserted into a system (Figure 1) and connected to CO_2 gas (from Martins PRAXAIR INC. WHITE^{TM}) with a concentration of 5000 ppm packaged in the cylinder, with a purity of 99.95%. For the experiments, a flux of 0.2 L/min was used with contact intervals of 5, 10, 15, 30, 45, and 60 minutes in the coalbed. Proximate analysis and ultimate analysis were measured before the tests and after the contact intervals between the CO_2-Coal interactions.

4. RESULTS AND DISCUSSION

The results of proximate analysis (Table 1) reveal that CO_2 injected into the coal changes its properties. The moisture and ashes underwent an increase of 5% after 60 minutes of the reaction. Also, an overall increase of 11% was observed for the volatile matter and fixed carbon. The ability of coal to adhere CO_2 releasing hydrocarbons manifests such behavior. The greater amount of CO_2 in contact with the charcoal bed produces greater ash content. The volatile matter has increased in content as a consequence of the increased amount of CO_2.

The ultimate analysis (table 1) results in an 8% increase for carbon and oxygen after 60 minutes of CO_2 flow in the coalbed. For sulfur, a decrease of 32% has been observed. This is due to the displacement capacity of sulfur in porous layers of coal. There was coal desulfurization with the increase of CO_2 flow during 60 minutes of contact.

5. CONCLUSIONS

The present study addressed the characteristics of the CO_2 capture and storage technique. In this context, a CO_2 injection scheme was presented in coalbed, and the physicochemical properties were verified after the experiments. It was established that according to the time of contact with the CO_2 flow, there is an increment of 5% of moisture and ash content and 6% of carbon and oxygen, in the coal. Subsequently, for the volatile matter and fixed carbon, there is a decrease of 7 and 11% respectively. The desulfurization caused by the injection of CO_2 into the coal where there was a 32% decrease is another interesting discovery.

Therefore, the results indicate that the proposed coalbed system was efficient in the adsorption of CO_2 and might act as an alternative for the removal of SO_2 in the coal.

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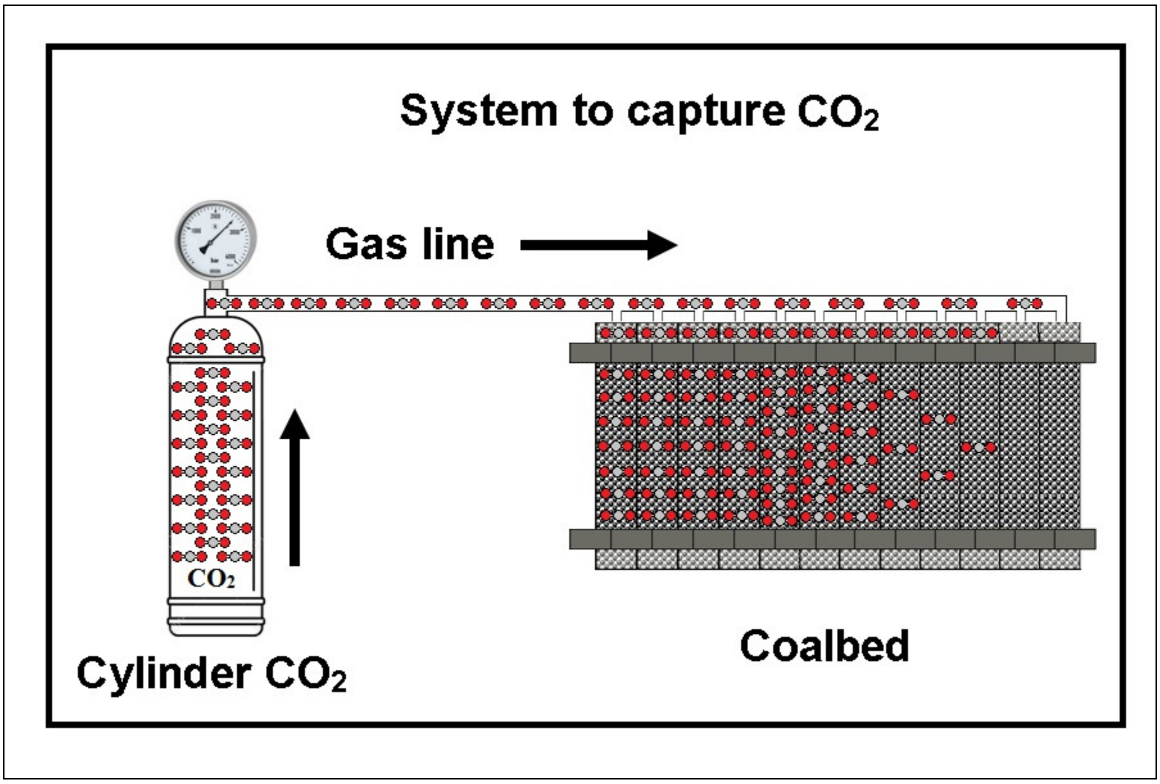

Figure 1. *Schematic system of capture CO_2 in coalbed*

Table 1: *Properties of the coal before and after interaction with carbon dioxide.*

Proximate analysis - Weight (%) on dry basis					
Samples	**Moisture**	**Ash**	**Volatile matter**	**Fixed carbon**	
CF	8.4	52.9	51.2	24.9	
C-5	8.7	53.4	51.7	25.7	
C-10	8.8	53.8	52.4	25.9	
C-15	8.8	54.2	52.6	26.3	
C-30	8.9	54.9	53.1	26.7	
C-45	9.1	55.3	55.9	27.5	
C-60	9.4	55.8	56.8	27.9	
Ultimate analysis - Weight (%) on wet basis					
Samples	**Carbon**	**Hydrogen**	**Nitrogen**	**Oxygen**	**Sulfur**
CF	25.4	4.9	0.9	14.9	2.5
C-5	25.7	5.0	0.9	15.1	2.3
C-10	26.0	5.2	0.8	15.3	2.0
C-15	26.3	5.2	0.8	15.4	1.8
C-30	26.8	5.3	0.8	15.7	1.6
C-45	26.9	5.3	0.8	15.9	1.4
C-60	27.3	5.3	0.8	16.1	1.1

CF (Coal free of CO_2 flux); C-5 (CO_2 flux in coalbed of 5 min); C-10 (CO_2 flux in coalbed of 10 min); C-15 (CO_2 flux in coalbed of 15 min); C-30 (CO_2 flux in coalbed of 30 min); C-45 (CO_2 flux in coalbed of 45 min); C-60 (CO_2 flux in coalbed of 60 min).

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

METHODOLOGY FOR DETERMINATION OF DEGREE OF NODULARITY IN A DUCTILE CAST IRON GGG 40 BY ULTRASONIC VELOCITY TEST

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ABSTRACT

Cast iron alloys combine many elements such as carbon, iron, silicon, magnesium and can be usually classified according to their microstructure in ductile, gray, compacted, white, and malleable. Each one has particularities in terms of properties and applications. Hence, this study aims to evaluate the degree of nodularity (%) in a ductile cast iron alloy GGG 40. In this context, a methodology to investigate the degree of nodularity was proposed. The ultrasonic method was used to determine the amount of ductile graphite as well as for parts release and thus facilitated the industrial operational execution. The effect of ultrasonic sound was investigated in sixty-seven ductile cast irons, and these analyses were further compared to the level of nodularity observed by metallography. Finally, based on the findings, the cast iron quality was guaranteed, leading to time-savings, avoiding the microstructural examination, and thus promoting cost reductions.

Keywords: *degree of nodularity, ductile cast iron, ultrasonic velocity test.*

1. INTRODUCTION

Ductile iron alloys have a highlighted position among all the other cast irons. One of its characteristics is to present carbon in the spheroidal graphite form (Skaland, 1993) to promote enhanced mechanical strength and ductility, which are essential properties in their practical applications. Their chemical composition is similar to the gray cast iron, containing more than 2% carbon. In particular, its spheroidal graphite is influenced by the magnesium addition, which is the nodularizing agent. Still, other elements may help in improving graphite shape (Davis, 1996; Guesser, 2009). One of the main problems faced by quality control in a foundry (cast iron) industry is to ensure that the product will not present an unwanted microstructure, the degree of nodularity is acceptable, and the parts can be used without problems (Wilccox, 2003). Several analyzes can be used for evaluating the cast iron quality and, often, microstructural evaluation is the first choice. However, for optimizing the manufacturing process, this analysis can be replaced by the ultrasonic test, providing higher efficiency and decreasing the material and time consumption.

The ultrasonic testing, although widely used in carbon steels, it was not yet commonly applied to cast irons (Wilccox, 2003). However, the production of ductile cast irons has grown in recent years. Therefore, in this field, these cast irons present some advantages, such as low manufacturing cost and easy fabrication (Herrera *et al.* 2013; Souza *et al.* 2014). As mentioned in (Gevaerd, 2007), the sonic velocity is a non-destructive test for analyzing cast irons, making it possible to correlate the microstructure with the sound propagating in the material. Being a versatile process, it can allow the release of large batches in reduced time. In this context, the sound

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velocity in a material depends on its microstructure, and there may be better or worse conditions for propagation. In addition, it should be noted that the graphite spheroidal shape presents less resistance to the passage of sound since the wave deflection is smaller (Gevaerd, 2007). Moreover, an error in Mg incorporation during the nodularization may lead to an unwanted structure. Hence, if the part presents a low sonic velocity, its inadequate degree of nodularity may lead to fracture due to insufficient material's strength. In this sense, some authors (Nabil, 2009) have mentioned that the main factors affecting the cast iron mechanical properties are related to its microstructure.

The industrial matter of this study was to release parts with an adequate microstructure and, consequently, to avoid the metallography step. Hence, for the parts to be approved, the degree of nodularity shall be greater than 80% (ASTM A247-17, 2017). This ductile graphite amount corresponds to a sonic velocity of 5595 m/s (Gevaerd, 2007), but for safety reasons, it is suggested that this sonic velocity shall be of 5603 m/s. On the other hand, when the evaluated samples reach sonic velocity values lower than it, a complementary microstructural evaluation is recommended.

2. MATERIALS AND METHODS

The chemical analyses were carried out in the optical emission spectrometer, as can be seen in Figure 1. Therefore, sixty-seven samples were taken into consideration.

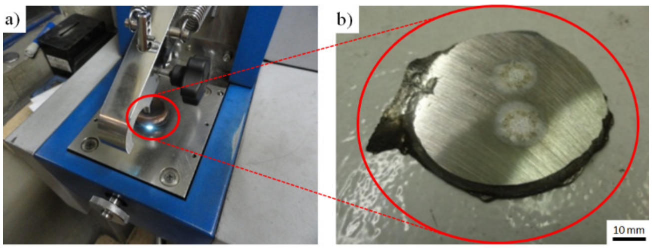

Figure 1. *a) Spectrometer, b) Sample.*

The study of sonic velocity and its relation with the degree of nodularity was performed in many specimens. The samples were randomly taken from batches, during the metal casting at a given fading time. In this context, Figure 2 a) presents the ultrasonic equipment used. The sonic velocity test was performed on specimens, as it is shown in Figure 2 b).

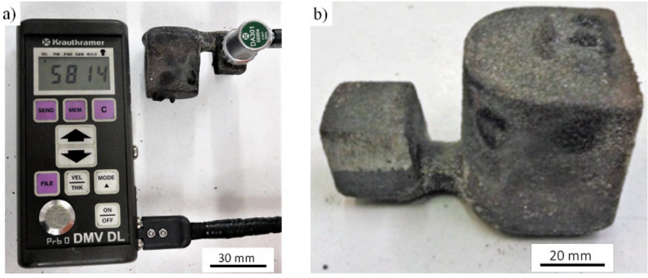

Figure 2. *a) Ultrasonic apparatus for sonic velocity test, b) Test specimen.*

The equipment, Krautkramer DMV DL Digital Ultrasonic Velocity Gauge, measures the pulse transit time and calculates the velocity (V) in which the sound propagates in the material as indicated by Equation 1. For correct measurements, it is important to know the sample thickness. After measuring the sonic velocity, a value that must guarantee a degree of nodularity higher than 80% is obtained and thus generating reliability in the desired microstructure.

$$V = \text{Distance travelled} / \text{Time [mm/s]} \qquad \text{(Eq. 1)}$$

For microstructural observation, samples were prepared by sample cutting, sandpaper, polishing, and then etched by Nital (2%). These samples were taken from sonic velocity specimens (Figure 3) and specific fading time, which was ranging from 8 to 10 minutes. Finally, the images were evaluated by Digimess software for verifying the level of nodularity.

Figure 3. *A test specimen for metallography.*

For tensile tests, cylindrical specimens were machined with Lo= 25 mm, as suggested by DIN 1563:2003 (DIN EN 1563, 2003), with dimensions as demonstrated in Figure 4. Hence, the mechanical tests were performed on an EMIC brand machine, according to ISO 6892 (NBR ISO 6892, 2013).

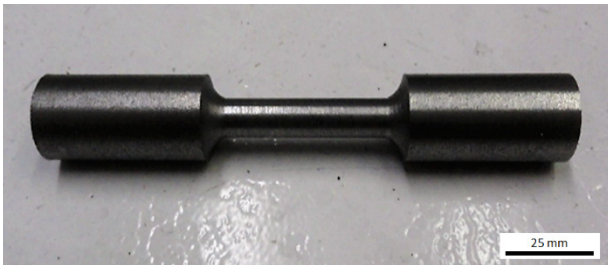

Figure 4. *A test specimen for the mechanical test.*

3. RESULTS AND DISCUSSIONS

Microstructural results, related to the degree of nodularity, sonic velocity and Mg content (%) for selected samples (6 samples with a degree of nodularity below 80%, and 6 samples with a level of nodularity greater than 80%) are shown in Figures 5, 6, 7 and 8. As different degrees of nodularity were obtained, they were classified into adequate (above 80%) and non-conformed (below 80%). In this sense, Figures 5 and 6 present the approved ductile cast irons, while Figures 7 and 8 display the unapproved ones, according to the methodology proposed. As reported in (Gevaerd, 2007), a sonic velocity of 5595 m/s caused a degree of nodularity of 80%, a fact which has a good agreement with the present study.

Figure 5 shows the cast iron microstructure in the spheroidal form and small-sized nodules. As the sonic velocity decreased (from 5662 m/s to 5641 m/s), the degree of nodularity decreased (from 91% to 86%). On the other hand, as can be seen in Figure 6, in general, as the sonic velocity decreases (from 5629 m/s to 5595 m/s), the level of nodularity increased (from 84% to 88%). This fact may be related to the Mg (%) content, which was shown to be variable in the samples (Figures 6 a), b) and c)).

Considering Figures 7 and 8, which present samples with a degree of nodularity below 80%, more heterogeneous microstructures were observed (in relation to graphite nodules). Moreover, Figure 7 shows nodules in different sizes and shapes. In addition, it was observed that as the sonic velocity decreased (from 5570 m/s to 5604 mm/s), the degree of nodularity decreased (from 75% to 48%), a fact that may be related to the nodules shape, some compacted and also veins. In fact, the graphite veins shape (also called graphite flakes) can act as a stress concentrator and maybe not favorable to the cast iron properties (Rudnev, 2018). Moreover, as verified in (Čanžar, 2012), the larger irregularly shaped nodules would promote unfavorable fatigue properties. Still, Figure 8 shows microstructures with similar behavior, where at a sonic velocity of 5017 m/s and Mg content of 0.008%, the lowest level of nodularity was achieved (17%).

Figure 9 presents a correlation between sonic velocities and degrees of nodularity. In this context, when the level of nodularity was greater than 80%, the sonic velocity values were close to the trend line (without great dispersion in the results). Conversely, for degrees of nodularity below than 80%, a greater difference was observed between sonic velocity values and levels of nodularity indicated by the trend line.

From the data presented in Figure 9, the means of the measurements were used to determine an equation that corresponds to the tendency observed in this work. Hence, Equation 2 represents these results. In this equation, the percentages of nodularity to obtain sonic velocities were applied (in the range of 17 to 100%). Thus, the approved samples (degree of nodularity above 80%) are presented in Table 1. From the practical foundry (cast iron) industry viewpoint, it can be revealed that this equation has been already used as a procedure for parts release.

$$y= -842{,}23x^3 + 1857{,}2x^2 -693{,}68x + 5393{,}3 \quad \text{(Eq.2)}$$

Figure 10 shows the correlation between the degree of nodularity (above 75%), (a) Ultimate Tensile Strength, (b) Elongation, and (c) Yield Strength. In general, as can be observed, these results showed that an increase in the degree of nodularity led to enhanced mechanical properties. On the other hand, for degrees of nodularity smaller than 75%, there was a large variation in the mechanical properties. Therefore, it indicates an inadequate microstructure and, consequently, these findings were not reported at this point.

Based on the current findings, the ductile cast iron batch release was done, considering a specified degree of nodularity of at least 80%, since it corresponds to the sonic velocity of 5595 m/s (Gevaerd, 2007). However, for safety reasons, it is suggested that the release shall be executed when sonic velocities higher than 5603 m/s are observed, applying the highest standard deviation verified (± 8 m/s). On the other hand, for sonic velocities below 5603 m/s, it is recommended that metallographic analysis must be performed for quantifying the real level of nodularity. Finally, it should be remembered that this non-destructive method can be applied as a practice for the evaluation of the degree of nodularity and, therefore, as a means of guaranteeing the quality required by ASTM A247 (ASTM, 2017).

4. CONCLUSIONS

The results of the present work, which proposed a methodology to determine the degree of nodularity by the sonic velocity in a ductile cast iron GGG 40, can be summarized as follow:

- The validation process for sonic velocity test and level of nodularity determination was important to obtain reliable results and subsequent release of ductile cast iron parts with reasonable quality.
- The nodular cast iron parts can only be released when sonic velocity higher than 5603 m/s are observed. For sonic velocities below of its value, it is necessary to observe the microstructural features in order to verify the real level of nodularity.

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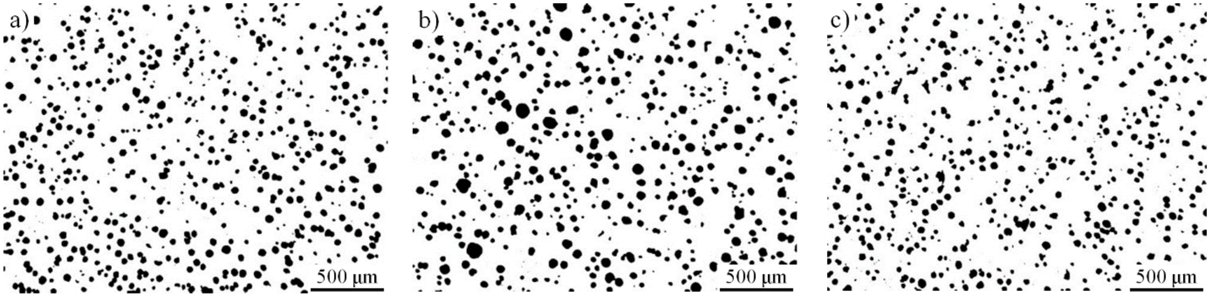

***Figure 5.** a) Degree of nodularity: 91%, sonic velocity: 5662 m/s, Mg: 0.026%. b) Degree of nodularity: 88%, sonic velocity: 5650 m/s, Mg: 0.025%. c) Degree of nodularity: 86%, Sonic velocity: 5641 m/s, Mg: 0.025%. 100X.*

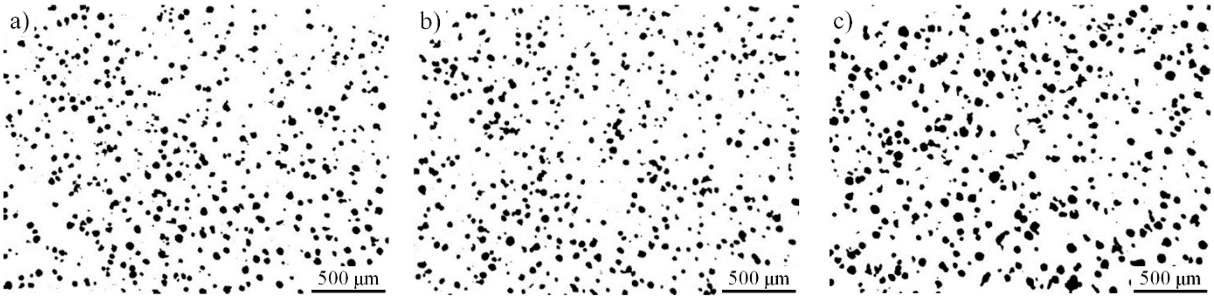

Figure 6. *a) Degree of nodularity: 84%, sonic velocity: 5629 m/s, Mg: 0.024%. b) Degree of nodularity: 82%, sonic velocity: 5610 m/s, Mg: 0.022%. c) Degree of nodularity: 78%, Sonic velocity: 5595 m/s, Mg: 0.019%. 100X.*

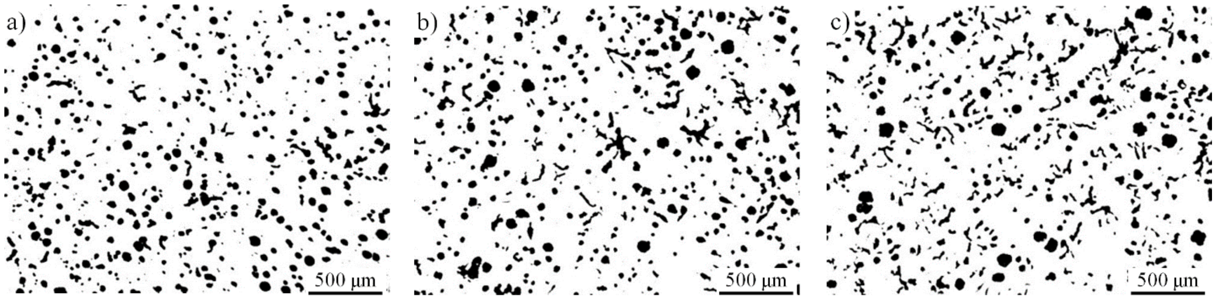

Figure 7. *a) Degree of nodularity: 75%, sonic velocity: 5570 m/s, Mg: 0.016%. b) Degree of nodularity: 65%, sonic velocity: 5462 m/s, Mg: 0.017%. c) Degree of nodularity: 48%, Sonic velocity: 5404 m/s, Mg: 0.016%. 100X.*

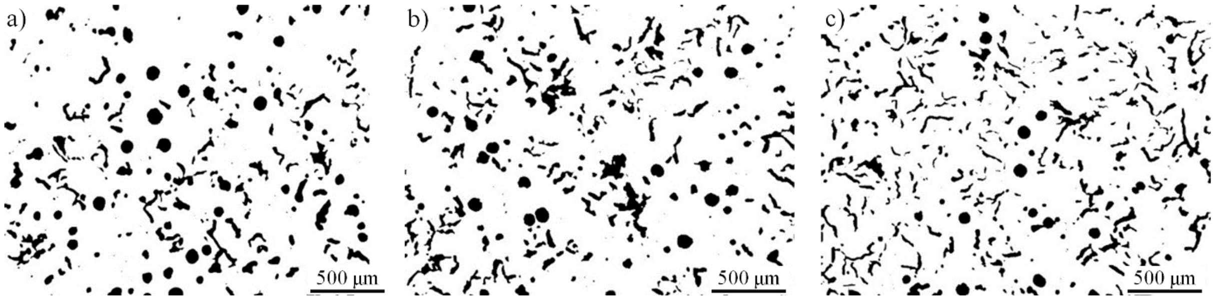

Figure 8. *a) Degree of nodularity: 45%, sonic velocity: 5373 m/s, Mg: 0.018%. b) Degree of nodularity: 33%, sonic velocity: 5335 m/s, Mg: 0.008%. c) Degree of nodularity: 17%, Sonic velocity: 5017 m/s, Mg: 0.008%. 100X.*

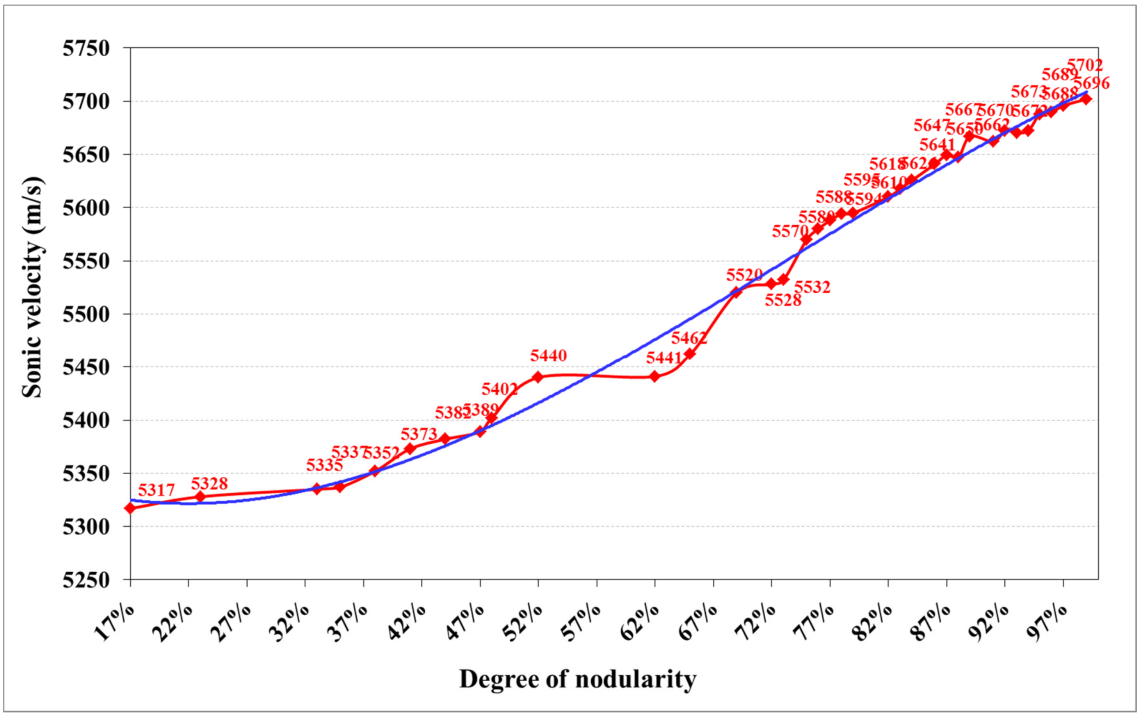

Figure 9. *Correlation between sonic velocity and degree of nodularity [%].*

Table 1. *The degree of nodularity (%) x Sonic Velocity.*

Nodularity [%]	Sonic velocity [mm/s]	Nodularity [%]	Sonic velocity [mm/s]	Nodularity [%]	Sonic velocity [mm/s]	Nodularity [%]	Sonic velocity [mm/s]
100%	5714	79%	5589	58%	5451	37%	5348
99%	5709	78%	5582	57%	5445	36%	5345
98%	5703	77%	5575	56%	5439	35%	5342
97%	5698	76%	5569	55%	5433	34%	5339
96%	5693	75%	5562	54%	5427	33%	5336
95%	5687	74%	5555	53%	5422	32%	5334
94%	5682	73%	5549	52%	5416	31%	5332
93%	5676	72%	5542	51%	5411	30%	5330
92%	5670	71%	5535	50%	5405	29%	5328
91%	5665	70%	5529	49%	5400	28%	5326
90%	5659	69%	5522	48%	5395	27%	5325
89%	5653	68%	5515	47%	5390	26%	5324
88%	5646	67%	5509	46%	5385	25%	5323
87%	5640	66%	5502	45%	5380	24%	5322
86%	5634	65%	5495	44%	5376	23%	5322
85%	5628	64%	5489	43%	5371	22%	5322
84%	5621	63%	5483	42%	5367	21%	5322
83%	5615	62%	5476	41%	5363	20%	5322
82%	5608	61%	5470	40%	5359	19%	5323
81%	5602	60%	5464	39%	5355	18%	5324
80%	5595	59%	5457	38%	5352	17%	5325

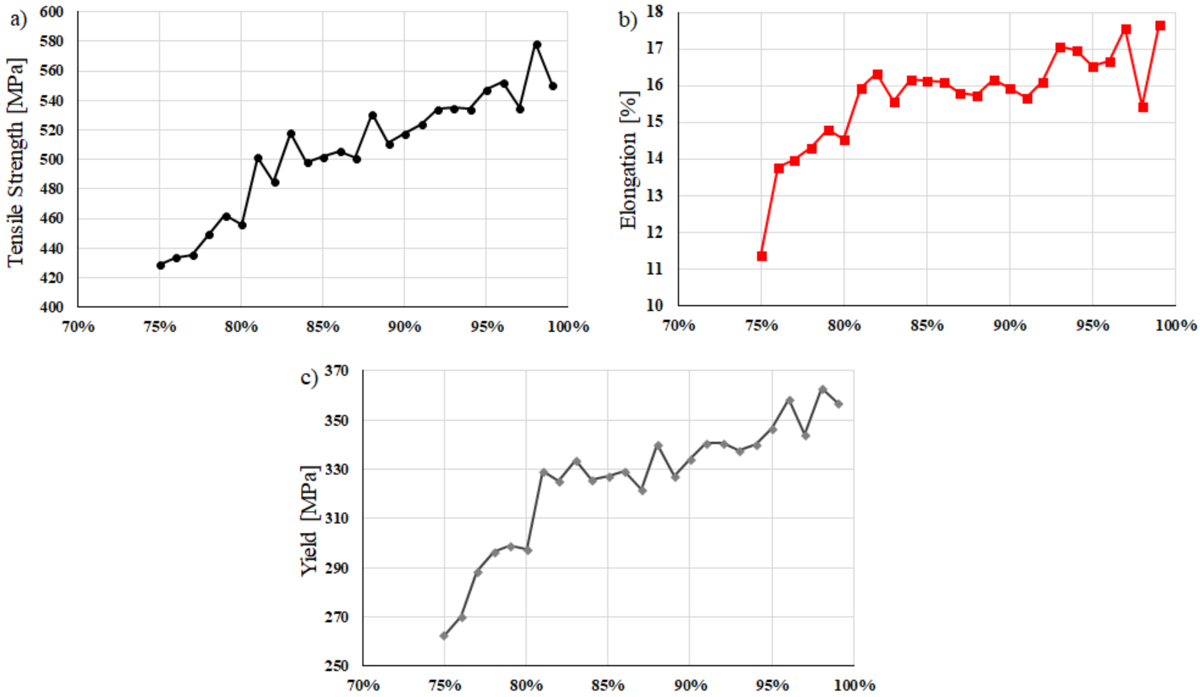

Figure 10. *Correlation between degree of nodularity and a) Ultimate Tensile Strength, b) Elongation, and c) Yield Strength.*

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

SLOW PYROLYSIS OF RICE STRAW: ANALYSIS OF BIOCHAR, BIO-OIL AND GAS

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ABSTRACT

Biomass is the term attributed to any renewable resource derived from organic matter that can be used in energy production. Agricultural production generates residues that are of great importance for their energy use, of which sugar cane, eucalyptus, and rice. Various residues are generated from rice cultivation, among which the rice husk and rice straw are the most important. Several thermal conversion technologies have been developed for the use of biomass in industry. Pyrolysis has been notable for its ability to produce biofuels at different stages of aggregation. The slow pyrolysis of biomass has been proposed as a pretreatment method to improve the physical-chemical characteristics of rice straw. In this process is produced, mainly, a solid called biochar, which has a higher energy content when compared to the biomass of origin. This study investigated the slow pyrolysis of rice straw at 300 - 700°C for the purpose of obtaining biochar, bio-oil, and gases for energy purposes. The experimental results show that pyrolysis temperature has important roles in yield product. The highest biochar yield was observed at a temperature of 300°C with 49.91 wt%. This represents 47% more when compared to yield at 700°C (33.87 wt.%). This behavior is linked to the proximate analysis results for fixed carbon 26.01 wt.% at 300°C. The high pH of the biochar was attributed to the presence of alkali metals, according to XRF. Thermal decomposition of the biomass resulting in a gradual increase of bio-oil (16.81 - 34.70 wt.%) and gas (6.53 - 18.05 wt.%) on a wet basis. Thus, in the dry base parameter, the bio-oil increases from 19.22 - 30.6 wt.% and the gases at 9.42-20.19 wt.%. Drying of the raw material showed, by the results, a significant increase in the co-products formed. As a consequence, we have a more efficient energy process.

Keywords: *Biomass, Pyrolysis Process, Renewable Energy, Biofuel, Tar*

1. INTRODUCTION

Thermochemical conversion technologies (pyrolysis, gasification, and combustion) have been developed for the use of biomass and applied in industry to produce different types of energy (Brown *et al.*, 2013; Bridgwater, 2012). Biomass is considered a potential for renewable energy sources in the future. Biomass can be categorized as agricultural waste being the only one among renewable energy resources that can be converted into an energy source (Jiang and Ellis, 2010).

The advantage of biomass in relation to fossil fuels is the low emission of sulfur and nitrogen (Carpenter *et al.*, 2014; Demirbas, 2011; Mohan *et al.*, 2006). The use of biomass as a source of renewable energy contributes to the mitigation of environmental impacts caused by greenhouse gas emissions (Jamilatun *et al.*, 2017, Lai *et al.,* 2013, Zhang *et al.*, 2012).

The pyrolysis of rice straw involves the thermal decomposition of polymer compounds, releasing organic vapors, and leaving carbon-rich solid residues (char) (Jahirul *et al.*, 2012). Pyrolytic vapors can be separated into condensable hydrocarbon compounds (oil, also known as tar) and non-condensable gases (Hosokai *et al.*, 2014).

The pyrolytic process is influenced by thermodynamic and kinetic parameters that alter the products. These parameters involve temperature, heating rate, particle size, reaction atmosphere, and residence time of the volatiles (Antal and Grønli, 2003).

Recent studies, published in the literature, bring the pyrolytic processes using rice straw (Zhang *et al.*, 2013, Chatterjee *et al.*, 2013, Huang *et al.*, 2013, Pattiya and Suttibak 2012; Fu *et al.*, 2012, Huang *et al.*, 2012, Wu *et al.*, 2012).

In this work, the use of pyrolysis is a process of thermal decomposition in the absence of oxygen or when the oxygen content is at an incomplete

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combustion level (Klunk and Ponomarev, 2017; 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). Fast pyrolysis is a well-studied technology that is reaching an early stage marketing (Jiang and Ellis, 2010; Effendi *et al.*, 2008). Fast pyrolysis technology has been investigated mainly for the production of bio-oil. It is typically performed using a fluidized bed to increase the heating rate (100°C / m) and at temperatures around 500°C to maximize the bio-oil yield. Higher temperatures and increased vapor residence time cause thermal cracking of hydrocarbon compounds, decreasing bio-oil yield (Klunk and Ponomarev, 2017, Zhang *et al.*, 2013, Eom *et al.*, 2013, Pattiya and Suttibak 2012). Unlike rapid pyrolysis, slow pyrolysis is carried out at a heating rate of about 5°C/min and temperature range of 300-700°C (Jamilatun *et al.*, 2017; Surahmanto *et al.*, 2017; Huang *et al.* , Wu *et al.*, 2012, Peng *et al.*, 2011).

The objective of slow pyrolysis in rice straw is the production of biochar and applicability in the soil with the purpose of increasing fertility. Biochar is responsible for increasing the retention of nutrients and water in the soil, providing the growth of microorganisms (Hossain *et al.*, 2011; Brockhoff *et al.*, 2010; Gaskin *et al.*, 2010). The amount of bio-oil and non-condensable gas products in terms of mass and energy is considerably larger than that for biochar (Kim *et al.*, 2012; Turns, 2011; Phan *et al.*, 2008).

Bio-oil is a renewable fuel or chemical feedstock, but its chemical properties are not as good as biochar due to its high water content and a large number of compounds resulting in acidity and toxicity (Agar and Wihersaari, 2012; Gómez et al. 2012). Pyrolytic gases are composed largely of CO and CO_2, leading to poor fuel quality.

This study presents the slow pyrolysis characteristics of rice straw to provide comprehensive information for the chemical properties and yields of the three pyrolysis products (biochar, bio-oil, and gases). The mass yield, elemental composition, and other key properties of the products were analyzed for pyrolysis temperatures of 300-700°C. Based on these results, considerations required for application of the slow pyrolysis technology to rice straw were discussed.

2. MATERIALS AND METHODS

2.1. Raw material

Rice straw was used as raw material, coming from a farm without pre-treatment. Proximate and ultimate analyses 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}). In this study, the ash content was measured by ASTM D1102-84. This requires gradual heating to 580–600°C repeated by 30 min periods until the sample weight does not change (<0.2 mg) (Jamilatun et al., 2017; Surahmanto et al., 2017; Huang et al., 2013; Wu et al., 2012; Peng et al., 2011).

2.2. Low pyrolysis

Low pyrolysis experiment of rice straw was carried out at temperatures of 300, 350, 400, 450, 500, 550, 600, 650, 700°C. The details of the reactor were described elsewhere (Lee *et al.*, 2013a). Three hundred grams sample of rice straw was placed in the reactor, and the experiments were carried out with a heating rate of 5°C/min. Nitrogen was continuously supplied at a flow rate of 2.0 L/min to purge pyrolysis vapors from the reactor. Once the reactor attained the target temperature, it was maintained for 1 h for complete pyrolysis.

Pyrolytic vapors containing condensable gases (bio-oil) and non-condensable gases passed through the condensers and the gas analysis system. The connection tube from the reactor to the bio-oil condensers was heated to 400°C. The biochar and bio-oil collected after the test was collected and weighed to determine the mass yields. The composition of gases was continuously analyzed by an on-line gas analyzer for CO and CO_2. The gas yield was calculated by difference. The mass yields on a wet basis were converted into a dry, ash-free basis to evaluate the product distribution from the organic fraction in biomass. The biochar yield was also converted to an ash-free basis.

3. RESULTS AND DISCUSSION

3.1. Product yields

Figure 1 represents the yields of the slow pyrolysis of rice straw in the temperature range of 300 to 700°C, on a wet basis (Fig. 1A) and dry basis (Fig. 1B).

On a wet basis, the biochar yield decreased with increasing temperature (Fig. 1A) ranging from 49.91 - 33.87 wt.%. This is due to thermal decomposition of the biomass, resulting in a gradual increase of bio-oil (16.81 - 34.70 wt.%) and gas (6.53 - 18.05 wt.%). The biochar yields include ash content that remained in the solid residue. In turn, the yield of bio-oil and gas have the contribution of moisture.

After the removal of moisture and ash content, the yield of the products had another behavior. Fig. 1B the biochar had a variation of 44.02 - 34.50 wt.%. Therefore, the bio-oil and gases yield varied from 19.22 - 30.6 wt.% and 9.42-20.19 wt.%, respectively. This can be results of cracking (secondary pyrolysis) of primary tar compounds by temperature and by hot char surface. Considering the significant influence of ash and moisture content in the raw material, it was desirable to convert the biochar yield to a dry, ash-free basis.

3.2. Biochar composition

Table 3 shows the properties of biochar. As the temperature of the pyrolytic process increases, the amount of volatile matter is expelled from the biomass (32.20 - 7.07 wt.%), making the material more carbonaceous (as a function of fixed carbon 26.01 wt.% at 300°C). In consequence, there is a decrease in the higher heating value from 15.80 MJ/kg to 8.77 MJ/kg, representing a reduction of 55%. The surface area (BET) increased from 3.91 to 43.39. This value is indicative of good adsorption capacity when applied to the soil. The surface area of the biochar from the 'rice straw' was relatively low when compared to the biochar of other lignocellulosic biomasses. For example, the biomass of wood and sugarcane bagasse is above 100 m^2/g (Lee *et al.*, 2013a, Lee *et al.*, 2013b). The pH of the bio-oil increased from 8.75 to 11.92. The alkalinity in rice straw is due to the presence of alkaline compounds (MgO, CaO, Na_2O, K_2O) according to the X-ray fluorescence (Table 2).

3.3. Bio-oil and gas composition

Table 3 summarizes the bio-oil properties for the mean of light organic and heavy organic phases. The bio-oil compounds were in Table , according to major individual compounds. Oxygenated compounds 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 30 to 23 wt.%. Ketones are the second largest organic group in the bio-oil. Ketones are formed by condensation reactions of the fraction derived from carbohydrates and decomposition of the various oxygenates and furans. When the pyrolysis temperature is increased, cracking reactions are more severe, and lighter compounds are formed. Acid functional groups have their highest yield, and the main compound of this group is acetic acid. 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.

The gas fraction is composed mainly of carbon dioxide and carbon monoxide (Table 4). The yields increase with temperature due to the increase in decarboxylation and decarbonylation reactions. In addition, this fraction is also composed of small amounts of hydrocarbons (C_2-C_4). The concentration of CO increases with temperature, while that of CO_2 decreases. This is because at temperatures below 400°C the decarboxylation reactions prevail, but at temperatures above 400°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 is a favorable environmental feature involving the RS pyrolysis process (Stefanidis *et al.*, 2011).

4. CONCLUSIONS

Rice straw is considered a high added value agricultural residue. Slow pyrolysis is the process responsible for this energy transformation. Co-products such as biochar, bio-oil, and gases are obtained with different yields at temperatures of 300 to 700 ° C due to the pyrolytic process. The experimental results show that pyrolysis temperature has important roles in the biochar, bio-oil, and gas yield.

The highest biochar yield was observed at a temperature of 300 ° C with 49.91 wt%. This represents 47% more when compared to yield at 700 ° C (33.87 wt.%). This behavior is linked to the results of "Proximate analysis" for fixed carbon 26.01 wt.% At 300 ° C). The high pH of the biochar was attributed to the presence of alkali metals, according to XRF.

The decomposition of lignocellulosic materials directly influences the contents of volatile matter (hemicellulose and cellulose decomposition) and fixed carbon (lignin decomposition)

Thermal decomposition of the biomass resulting in a gradual increase of bio-oil (16.81 - 34.70 wt.%) And gas (6.53 - 18.05 wt.%) In wet basis. Thus, in the dry base parameter, the bio-oil increases from 19.22 - 30.6 wt.% and the gases at 9.42-20.19 wt.%. The gas yields increase the temperature increases in the 300-700°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. Drying of the raw material showed, by the results, a significant increase in the co-products formed. As a result, we have a more efficient energy processes.

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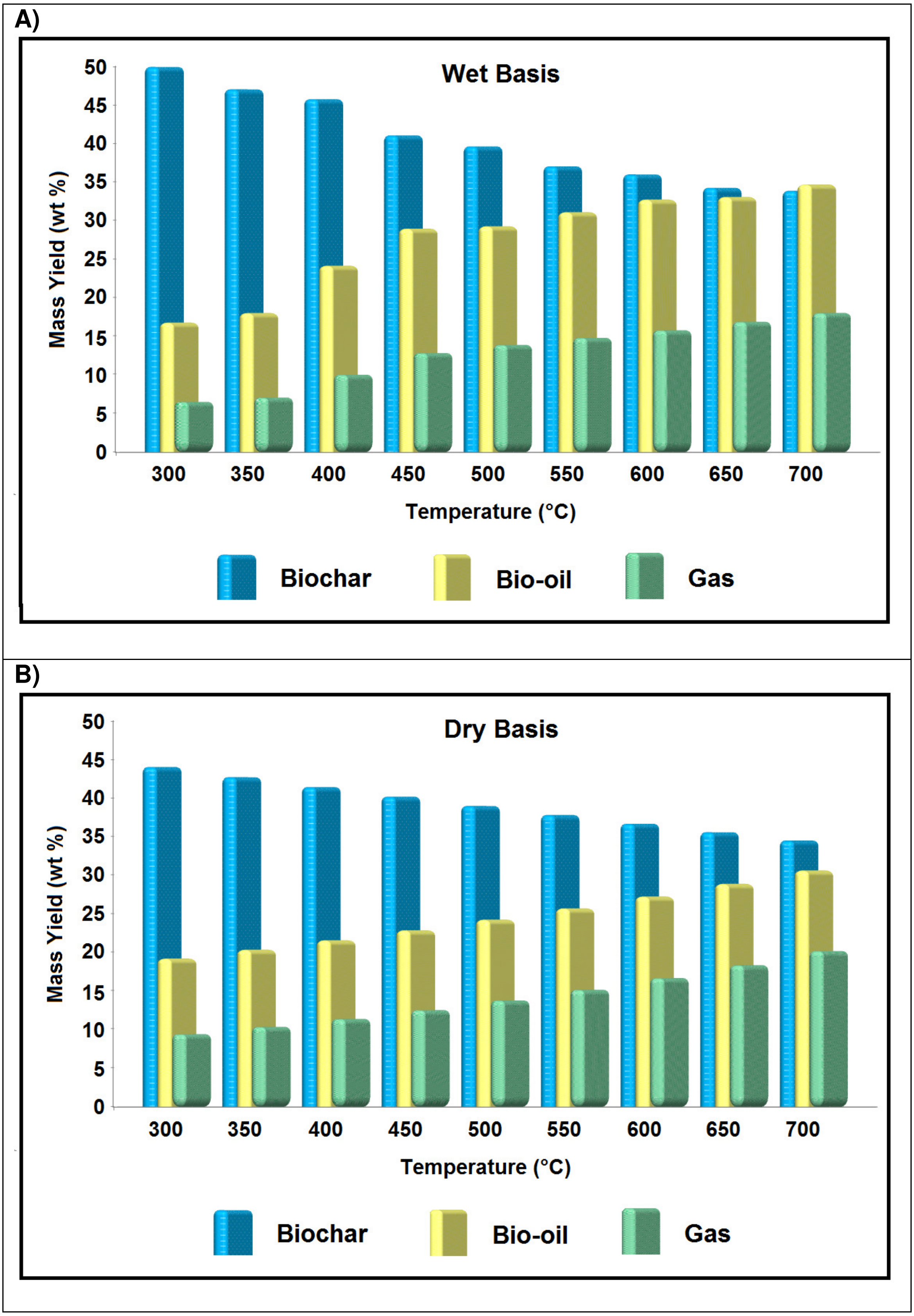

Figure 1. *Product yield From slow pyrolysis of rice straw, A) on wet basis and B) dry basis*

Table 1. *Properties of the rice straw*

Proximate analysis		**Ultimate analysis**	
Parameters	**Weight (%) on dry basis**	**Elements**	**Weight (%) on wet basis**
Volatile matter	65.71	Carbon	50.59
Fixed carbon	15.13	Hydrogen	7.02
Ash	14.29	Nitrogen	2.55
Moisture	6.41	Oxygen	48.10
HHV* (MJ/kg)	20.88		

*HHV: Higher Heating Value

Table 2. *Chemical composition of the rice straw ash*

Compound	**Weight (%)**
SiO_2	71.82
Al_2O_3	1.55
Fe_2O_3	0.28
MnO	0.01
MgO	4.99
CaO	3.03
Na_2O	0.20
K_2O	0.15
TiO_2	0.02
P_2O_5	0.09
Loss on ignition	10.99

Table 3. *Properties of the biochar*

P.T [a]		**300 (°C)**	**350 (°C)**	**400 (°C)**	**450 (°C)**	**500 (°C)**	**550 (°C)**	**600 (°C)**	**650 (°C)**	**700 (°C)**
P.A [b]	VM	32.20	30.17	22.39	20.71	15.40	13.44	9.92	8.41	7.07
	FC	26.01	25.64	23.88	21.08	20.99	19.85	18.13	20.48	22.01
	Ash	35.55	36.87	39.90	41.07	46.10	47.53	49.60	50.39	52.97
U.A [c]	C	63.34	65.08	69.72	70.83	77.53	78,66	80,61	82.07	86.62
	H	3.79	3.00	2.44	2.20	1.97	1.21	1.01	0.92	0.82
	N	2.99	2.81	2.32	2.09	1.83	1.68	1.40	1.09	0.79
	O	20.81	18.90	16.73	15.05	13.92	12.62	8.83	7.53	6.98
HHV [d]		15.80	14.77	13,92	12.54	11,96	10.66	9.77	9.00	8.77
BET [e]		3.91	11.88	19,70	36.63	40.81	44.49	59.58	50.72	43.39
APD [f]		100.4	99.03	85.42	83.74	81.79	79.92	78.00	76.64	75.07
PV [g]		0.027	0.038	0.041	0.044	0.048	0.050	0.052	0.054	0.055
pH		8.75	9.10	9.55	9.93	10.10	10.99	11.15	11.30	11.92

[a] Pyrolysis temperature; [b] *Proximate analysis;* [c] *Ultimate analysis;* [d] *Higher Heating Value (MJ/kg-dry);* [e] *Surface area (m_2/g);* [f] *Average pore diameter (Å); Pore volume (cm^3/g);* [1] *Volatile matter;* [2] *Fixed carbon;* [3] *Carbon;* [4] *Hydrogen;* [5] *Nitrogen;* [6] *Oxygen*

Table 4. *Yields of the main chemical compounds in the bio-oil*

Compounds	**300 (°C)**	**350 (°C)**	**400 (°C)**	**450 (°C)**	**500 (°C)**	**550 (°C)**	**600 (°C)**	**650 (°C)**	**700 (°C)**
Acetic acid	2.30	2.33	2.38	3.40	2.32	2.42	2.53	2.85	2.92
Propanoic acid	1.26	1.39	1.45	0.92	0.29	0.29	0.30	0.28	0.20
Formaldehyde	0.28	0.30	0.30	0.47	0.49	0.50	0.57	0.68	0.74
1-Hydroxy-2-propanone	1.98	1.77	1.58	1.32	0.89	0.72	0.43	0.31	0.22
1,3-Cyclopentanedione	3.88	3.52	3.14	2.67	2.59	1.90	0.81	0.77	0.65
2-3-methyl-2-cyclopentenone	1.34	1.30	1.19	1.18	1.38	1.31	0.42	0.36	0.29
Alkyl-phenols	2.99	3.09	3.07	3.72	3.77	3.96	6.62	6.99	7.03
Guaiacols	4.79	4.50	3.91	3.32	2.84	2.80	2.74	2.38	2.00
Catechols	1.44	2.00	2.90	3.34	3.42	3.50	3.76	4.01	4.17
2,2,4-Trimethyl-1,3-dioxalane	3.06	2.89	2.41	2.30	1.65	1.52	0.97	0.88	0.54
Carboxylic Anhydrides	1.83	1.44	1.19	1.09	1.01	1.08	1.10	1.33	1.45
Furans	4.03	4.37	4.39	4.65	5.12	4.85	4.24	4.00	3.83
Nitrogenated compounds	0.90	1.00	1.08	1.36	1.61	1.34	1.11	1.09	0.97
Water	30.92	27.99	26.32	24.27	24.52	24.61	25.21	24.54	23.12

Table 5. *Influence of temperature on gas composition*

Compounds	**300 (°C)**	**350 (°C)**	**400 (°C)**	**450 (°C)**	**500 (°C)**	**550 (°C)**	**600 (°C)**	**650 (°C)**	**700 (°C)**
H_2	0.73	0.99	1.45	1.55	1.95	2.85	3.52	3.99	4.39
CH_4	2.56	2.74	3.44	3.73	5.30	5.99	7.92	10.55	10.69
CO	49.31	51.35	54.41	55.49	57.20	58.86	59.30	60.51	61.88
CO_2	55.12	54.07	52.93	50.38	47.62	45.06	40.87	38.92	35.57
C_2-C_4	1.55	2.98	3.73	4.55	4.97	5.67	5.99	6.48	6.93

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

STUDY OF ALAZANI RIVER AND SURFACE WATER COMPOSITION IN SOME VILLAGES OF KAKHETI REGION OF GEORGIA

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ABSTRACT

The article reviews the chemical composition of borehole and surface waters in three villages of one of the regions of Georgia - Kakheti, Gurjaani Municipality. The study was specifically focused on iodine content in waters. It turned out that certain amount of iodine really existed in borehole waters, which means that by everyday drinking of water, the human body gets maybe not the complete required amount of iodine, but at least some part of it. It was also discovered, that according to certain parameters, waters are clean, do not contain heavy metals and can be freely used for drinking and cooking. The chemical composition of the Alazani River was also examined according to all four seasons. This river is interesting because of being used for irrigation of vineyards and fruit gardens.

Keywords: *Georgia waters, environmental chemistry; river pollutants, drinking water.*

1. INTRODUCTION

Water cleanliness is of particular importance nowadays. This is conditioned by the fact that pollutants from water directly penetrate into the human body. Through underground waters they flow into the ground, ultimately getting into surface waters. From there, they might be found in the atmosphere through deodorants

The purpose of our job was to study surface and borehole waters in some villages of Gurjaani region [1].

Gurjaani is a municipality of Kakheti region in east Georgia. The territory of Gurjaani municipality belongs to moderate humid subtropical climate zone. The moderately humid climate is developed on the plain in the east, with moderately cold winter and hot summer. There is a moderately humid climate on Gombori ridge, with long summers. The average annual temperature is 12,4°C, the average temperature of the coldest month – January is 0,11C, and of the hottest month – August - 35.8°C. Average annual precipitation on the major part of the territory is up to 800mm, ultimately decreasing to 500-600mm in the direction of the plateau.

Generally, water is not a problem in the villages of Gurjaani region. Water scarcity might be the case in any season. At this time, water in rural community tap is actually dependent on rainfall. Waters themselves flow down from mountains and gather in a catchment, with no treatment plant functional. Such plants might exist in some of the villages, though very outdated and needing repairs. Therefore, population avoids drinking the tap water.

There is no centralized wastewater system in villages; accordingly, affluent waters are not treated as, for instance, in neighbor countries [2]. As for rural spring waters, they are the so called borehole waters, originating from the top of the mountains. They do not gather in any catchment, but rather flowing down straight to the designated area (or to privately owned yards or village streets for common use) through the forest, being naturally filtered in the moss. The population drinks them directly (Fig.1; 2; 3). The water running to the village (running from community

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taps) is used for washing (including, for washing food products) and watering the house gardens.

Figure 1. Borehole water in one of the village dwellers' yards (village Vazisubani)

Figure 2. Borehole water in village street (Village Kalauri)

Figure 3. Borehole water on the highway (Village Chalaubani)

Figure 4. Alazani River

The chemical composition of the Alazani river (Figure 4) was also studied during the research process. It is one of the significant rivers of east Georgia, with a length of 390 km, catchment area – 11800 sq.km. River head is located on the Greater Caucasus mountain range, on the eastern slope of peak Great Borbalo. In the upstream it is a mountain river, flowing down to Alazani valley, developing the branches and joining the Mingechauri Reservoir (Azerbaijani). Before reservoir construction, Alazani used to stream down directly into Mtkvari River. Adjacent planes of the Alazani River belong to the vinegrowing municipality, and the river is used for irrigation. Interestingly, here, one can find different varieties of grapes (Rkatsiteli, Mtsvane, Cabernet, Saperavi, etc.). The banks of Alazani River are covered by cultivated strawberry and peach gardens. That's why we are interested in the ecological condition of Alazani, as, in case of its pollution, it can contaminate food products as well. Unfavorable ecological condition of Alazani River may be resulted by untreated affluent municipal waters, as well as by drainage runoff from agricultural lands. The river is also significantly contaminated by existing legal and illegal landfills, often located on river banks [3,4,5].

It should be noted that polluted landfill left-over waters are extremely toxic for water ecosystems, containing both organic substances, heavy metals, and other dangerous components. The river is used for irrigation of agricultural crops without any specific biological and chemical treatment. In this case, the whole polluted water body is filtered in the soil, enriching it with both heavy metals and various toxic compounds, often posing a threat of polluting the products, especially the vegetables cultivated in this zone.

2. MATERIALS AND METHODS

Samples were taken throughout the year of 2018, during all the four seasons of the year, but not in all cases. Iodine samples were taken in all four seasons.

5 samples were taken from the village Vazisubani. From there, 4- from borehole water and one from rural surface water.

Three samples were taken from the village Kalauri. Out of them, 2 were taken from borehole water and one-from rural surface water.

Two samples were taken from village Chalaubani, both of them from borehole water.Mainly the following parameters were examined: pH; Carbonate hardness; Common acidity, general acidity; Presence of Sulfate and chloride ions; the existence of some heavy metals and iodine samples. The main physiological function of iodine is to participate in the metabolism of hormones produced by the thyroid gland. Thyroid and breast glands are characterized by the ability to accumulate iodine. Its accumulation is also visible in saliva. Iodine deficiency is characterized by a number of symptoms: weakness, skin jaundice, feeling of cold, hair loss, irritability, frequent fatigue, memory loss, and finally, the most important development of feeble-mindedness [6,7,8].

Nowadays, world medicine has found the easiest and cheapest way of getting iodine, which means iodine supplementation in the salt, i.e., the use of iodized salt. However, this is also a disputable issue, because the same salt needs to be stored in a remote place away from sunlight to prevent iodine disintegration. It can be done at home, but we do not know in what conditions the salt was stored or transported before getting placed on supermarket shelves. Even if we assume that iodine really exists in salt and is not disintegrated, eating large amounts of salt creates other, not less dangerous problems to the body. Thus, we should be looking for other additional natural ways of getting iodine both from products and water [9].

It's a common knowledge that one of the reasons causing goiter disease is iodine deficiency in potable water. It is established that in the places where one liter of potable water contains 0,0001-0,001mg iodine, i.e., 0,1-1,0 mg, from 1000 people 15-30 men get diseased with goiter. Where iodine content reaches 0.001-0,01mg in a liter, from 1000, only two-three disease cases are registered [10,11,12].

Borehole water studies have shown that waters contain different quantities of iodine in different periods of the year. It depends on a number of conditions, for instance, on rocks, from which the spring is flowing down, on atmospheric conditions, on time, on soil type, etc.

Deriving from the above mentioned, we've explored iodine content in surface waters of the aforementioned villages. Iodine was defined through the following method [13,14,15,16,17]: iodides were oxidized through bromine water till getting iodates, and the segregated iodine was determined by the iodometric method:

$I^- + 3OBr^- \rightarrow IO_3^- + 3Br^-$
$IO_3^- + 6H^+ + 6I^- \rightarrow I^- + 3I_2 + 3H_2O$
$3I_2 + 6S_2O_3^- \rightarrow 3\ S_4O_6^{2-} + 6\ I^-$

Basically, we applied the methods of quantitative analysis for defining other parameters (total hardness, alkalinity, acidity). Through quantitative analysis, we also determined nitrates, nitrites, and sulfate ions. Chlorine defining method was based on chlorine-ion titration with a solution of mercury nitrate in the presence of indicator dyphynill carbasone. During titration, Mercury ions join chlorine ions and produce slightly dissociating HgCl2. And excess ions of mercury produce complex purple compounds with indicator dyphynill carbasone.

In the course of the experiment, we determined some of the metals: TS EN ISO 7294-2, TS EN ISO 11885. pH, temperature, conductivity, and suspended solids were measured on site, through methods SM 4500 H^+ B, SM 2550 B and SM 2540 D. [18,19,20]. Obtained results are given in tables #1-8. Samples from Alazani were taken in spring and summer from the points descending into the river from Village Vazisubani. See the results in Table #9

3. RESULTS AND DISCUSSIONS

Carbonate hardness of examined waters is within the norms. However, it can be said that they have hardness. Compared to borehole waters, hardness is higher in village tap waters. General alkalinity and acidity are much less compared to the norm. However, their indicator in rural village surface waters is significantly higher compared to borehole waters. The maximum indicator was observed in the summer season. It is significant that the quantity of ammonium ion, nitrates, and nitrites is minimal. This means that anthropogenic contamination should be completely excluded. As for the sulfate ions, they do not exist in borehole waters. A very little amount was observed in rural tap water. Hereby we note, that there is a very low indicator of aluminum in waters and it does not exist in the form of sulfate. Aluminum may get into surface and underground waters through affluent waters. There is no central wastewater system in villages and used rural surface water flows down to the ground. Aluminum sulfate might get into wastewater through cheap household chemistry, shower gels, shampoo, washing jellies). However, in our case, sulfate ions in rural surface waters are present in insignificant amounts, but they are completely absent in borehole waters, which means that no mixing or water contamination takes place there.

As for other metals, copper exists in rural surface water in little amounts. Presumably, water is polluted in catchments, where rural surface water is collected before running into the village. Iron is present in all types of water in little quantities, and we assume that it might be caused by pipes. Lead and manganese aren't measured anywhere.

It is notable that no metal is observed in borehole waters of village Chalaubani. These waters are channeled on the main road, where numerous passengers and tourists use to stop. Pipes, where water flows from, are made of stainless steel.

We haven't measured the hazardous heavy metals in any sample, such as mercury and cadmium (lead belongs to the group, we measured). Although we conducted the reactions to discover these metals, their existence was not revealed.

As for iodine content, it is observed in examined rural borehole waters in certain amounts. Sometimes it is absent, or present in very little quantities in rural tap waters.

According to seasons of the year, iodine is more in samples taken in summer (especially April-May), which probably is related to intensive washout of substances included in rocks due to rainfall in these months.

For a comprehensive assessment of Alazani river ecological condition, we considered it relevant to study the process of its mineralization. As the studies showed, the river is characterized by average mineralization near Vazisubani area, with the value varying between 140-160 mg/l. The following ions are found in water HCO^{-3}, Cl^-, SO_4^2, Ca^{2+} , Na^+ , Mg^{2+} etc.

There is an anthropogenic impact. For instance, the wastewater system in Gurjaani is not in good working conditions or represents an open sewage system; their ravines are used as landfills and the coastline - as a "resting place" for animals, therefore, they play a big role in polluting the Alazani River. As a result of observation, it was established that cation concentrations in the Alazani River increase streamwise and do not exceed maximum permissible concentration. As for SO_4^{2-} and Cl ions, they increase, indicating an intensification of anthropogenic impacts, fecal contamination, and eutrophication process. Compositions of biogenic elements (NO_2^-, NO_3^-), increasing streamwise, reach the maximum value in Gurjaani, where their concentrations are number of times more than 0.002 mg/l.

On the whole, pollution of the Alazani River does not go beyond the norm. In our opinion, it happens thanks to self-purification of the river. During this time, water more or less regains the original chemical and bacteriological composition.

This is facilitated by the turbulent flow of Mountain Rivers and good aeration. In addition, increased turbidity creates favorable conditions for sorption purification of water.

4. CONCLUSIONS

As a result of the research conducted, borehole waters in Gurjaani municipality villages – Chalaubani, Kalauri, Vazisubani, are of good quality and can be used for drinking. In addition, a certain amount of iodine was observed in the inspected borehole waters, which means that drinking these waters is also useful for health.

It is preferable to abstain from drinking rural surface waters. However they can be used for irrigation and washing purposes.

Alazani River studies have shown that, on the whole, its pollution is within the norms and presumably this is achieved by self-purification of the river.

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Table 1. Some parameters of borehole and surface waters in village Vazisubani

village Vazisubani	**Unit**	**Standard**	**Sample1 (Borehole water)**		**Sample 2 (Borehole water)**		**Sample 3 (Borehole water)**		**Sample 4 (Borehole water)**		**Sample 5 (Vilaage Water)**	
			Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
pH	-	6-9	7.8	6.2	8.7	8.4	7.9	6.1	8.0	7.6	9.3	6.1
Conductivity	µS/cm	<2500	140	111	101	98	120	73	90	63	87	69
Color	Pt-Co	<10	-	-	-	-	-	-	-	-	8	5
Temperature ºC	ºC		17	6	16	8	13	5	15	8	23	5
Suspended Solid	mg/L		-	-	-	-	-	-	-	-	-	<2
Total Hardness	mg/L	<50	9.0	7.6	10.2	8.1	15.4	8.2	12.02	9.1	20,1	14,3
Sulfat (SO_4)	mg/L	<250	-	-	-	-	-	-	-	-	0,57	0.23
Alkalinity	mg/L	<200	3,85	2,01	3,5	1,97	2,18	2,02	2,0	0,34	4,18	4,2
Acidity	mg/L	<300	0,7	0,54	0,67	0,53	1,8	1,06	1,07	0,52	3,8	1,63
NH4	mg/L	0.2	0,08	0.01	0.12	0.02	0,07	0.02	0,1	0.011	0.2	0.04
Ammonia Nitrogen (NH3-N)	mg/L	0.2	0.1	0.01	0.1	0.01	0.32	0.05	0.2	0.01	0.2	0.07
Cl	mg/L	250	5.0	4.0	23.8	15.9	37.2	32.1	29.0	22.8	54.1	21.6

Table 2. Some metals of borehole and surface waters in village Vazisubani

village Vazisubani	Unit	Standard	Sample1 (Borehole water)		Sample 2 (Borehole water)		Sample 3 (Borehole water)		Sample 4 (Borehole water)		Sample 5 (Vilaage Water)	
			Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Al	µg/L	1-200	1.0	0	0.5	0.2	0.3	0.01	1.2	1	13.8	9.0
Cu	µg/L	100	-	-	-	-	-	-	-	-	14	9
Fe	mg/L	0.2	0.13	0.01	0.11	0	0.11	0.1	0.09	0.02	0.21	0.11
Pb	µg/L	10	-	-	-	-	-	-	-	-	-	-
Mn	µg/L	50	-	-	-	-	-	-	-	-	-	-

Table 3. Some parameters of borehole and surface waters in village Kalauri

village Kalauri	Unit	Standard	Sample1 (Borehole water)		Sample 2 (Borehole water)		Sample 3 (Vilaage Water)	
			Max	Min	Max	Min	Max	Min
pH	-	6-9	7.2	4.1	8	7.4	7.2	5.01
Conductivity	µS/cm	<2500	120	88	131	69	120	53
Color	Pt-Co	<10	-	-	-	-	8	4
Temperature ºC	ºC		15	7	14	4	19	7
Suspended Solid	mg/L		-	-	-	-	-	<1.5
Total Hardness	mg/L	<50	8.0	6.1	12.0	9.3	18.7	6.02
Sulfat (SO_4)	mg/L	<250	-	-	-	-	1.0	0.45
Alkalinity	mg/L	<200	2.0	0.04	2,0	0,25	8,98	9,02
Acidity	mg/L	<300	1,07	1,02	1.5	0,65	0,9	0,99
NH4	mg/L	0.2	0,01	0	0,01	0.014	0.09	0.03
Ammonia Nitrogen (NH3-N)	mg/L	0.2	0.56	0.07	0.2	0.1	0.2	0.09
Cl	mg/L	250	8	7	11.8	5.7	43.7	35.2

Table 4. Some metals of borehole and surface waters in village Kalauri

village Kalauri	**Unit**	**Standard**	**Sample1 (Borehole water)**		**Sample 2 (Borehole water)**		**Sample 3 (Vilaage Water)**	
			Max	Min	Max	Min	Max	Min
Al	µg/L	1-200	1.2	0.9	1.89	1. 34	18.7	7.9
Cu	µg/L	100	-	-	-	-	12	8
Fe	mg/L	0.2	1.1	0.05	0.2	0.01	0.43	0.14
Pb	µg/L	10	-	-	-	-	-	-
Mn	µg/L	50	-	-	-	-	-	-

Table 5. Some parameters and metals of borehole and surface waters in village Chalaubani

village Chalaubani	**Unit**	**Standard**	**Sample1 (Borehole water)**		**Sample 2 (Borehole water)**	
			Max	Min	Max	Min
pH	-	6-9	6	6.7	8.01	8.05
Conductivity	µS/cm	<2500	57	34	45	23
Color	Pt-Co	<10	-	-	-	-
Temperature ºC	ºC		5	3	7	2
Suspended Solid	mg/L		-	-	-	-
Total Hardness	mg/L	<50	2.9	2.0	3.7	3.0
Sulfat (SO_4)	mg/L	<250	-	-	-	-
Alkalinity	mg/L	<200	43	12	32	16
Acidity	mg/L	<300	1.98	1.0	2.8	0.97
NH4	mg/L	0.2	-	-	-	-
Ammonia Nitrogen (NH3-N)	mg/L	0.2	-	-	-	-
Cl	mg/L	250	114.5	48.6	23.8	8.1
Al	µg/L	1-200	-	-	-	-
Cu	µg/L	100	-	-	-	-
Fe	mg/L	0.2	-	-	-	-
Pb	µg/L	10	-	-	-	-
Mn	µg/L	50	-	-	-	-

Table 6. Iodine content borehole and surface waters in village Vazisubani

village Vazisubani	Unit	Standard	Winter	Spring	Summer	Autumn	Average
	µg/L	4-18					
Sample1 (Borehole water)			2.4	19.4	18.5	3.2	10.8
Sample2 (Borehole water)			1.1	11.0	9.7	12.8	8.7
Sample3 (Borehole water)			0.8	5.3	5.0	8.6	3.4
Sample4 (Borehole water)			8.2	25.0	4.1	21.5	12.0
Sample 5 (Vilaage Water)			0.2	0.9	0.4	-	0.37

Table 7. Iodine content borehole and surface waters in village Kalauri

village Kalauri	Unit	Standard	Winter	Spring	Summer	Autumn	Average
	µg/L	4-18					
Sample1 (Borehole water)			8.9	15.0	13.2	12.8	12.4
Sample2 (Borehole water)			5.6	16.0	13.8	12.6	12.0
Sample 3 (Vilaage Water)			0.9	2.9	2.4	3.5	2.4

Table 8. Iodine content borehole waters in village Chalaubani

village Chalaubani	Unit	Standard	Winter	Spring	Summer	Autumn	Average
	µg/L	4-18					
Sample1 (Borehole water)			6.9	17.0	10.0	3.8	8.7
Sample2 (Borehole water)			13.5	7.0	3.2	4.2	4.4

Table 9. Some parameters from Alazani River

Some parameters from Alazani River	Gurjaani	
	Spring	Summer
Odor (in scores)	0	0
Color	20	20
Transparency	8.0	8.9
pH	7.9	8.3
BOD	7.2	6.5
Suspended substances	79	80

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

WASTE FRYING OIL TRANSESTERIFICATION TREATED BY STEAM DRAG METHOD

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ABSTRACT

Demand for diversified biodiesel feedstocks is high and increasing, but few are viable for large-scale production, and many of those selected compete with other sectors of the chemical industry. To improve energy and environmental sustainability, fatty acids from waste oils that are improperly disposed of and pollute the environment can be used for transesterification reactions. However, they need treatment to achieve high conversion rates. In this context, the aim of this work was to perform and analyze the treatment of residual frying oil with the evaporation and entrainment process, aiming at its use as raw material to obtain biodiesel (methyl esters) by a transesterification reaction. The physicochemical properties of the residual oil after treatment were characterized by moisture content, pH and the acidity, saponification, iodine, and peroxide index. The conversion rate of the residual oil to methyl esters was determined by ^{1}H NMR analysis. After the treatment, the method of analysis of variance showed that the oil obtained a significant reduction of the saponification, iodine, peroxide and acidity indexes, being the acidity reduced from 9.36 to 7.85 mg KOH g^{-1}. The moisture content of 0.733 % and elevation of pH to 8.0. The conversion rate of fatty acid biodiesel of residual oil was 79.3 %, lower value of standards norms (ASTM, 2005; EN, 2008; ANP, 2014), showing that the assigned methodology for frying residual oil is inefficient in biodiesel production.

Keywords: *Fatty acid, Biodiesel, Analysis of variance, Standards norms*.

1 INTRODUCTION

The interest of alternative and renewable sources for the production of biofuels as a renewable energy resource has been intensified over the years to gradually soften the social, environmental and economical energy problems caused by fossil fuels (Marcossi e Moreno-Perez, 2017; Jain *et al*., 2018).

Biomass, considered as a renewable source of energy, is used in the production of biofuels such as biodiesel. Biodiesel is defined internationally by the American Society for Testing and Materials (ASTM) as a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel can be produced by several methods, the transesterification reaction of triglycerides with short-chain alcohol (methanol and ethanol) in the presence of a homogeneous or heterogeneous catalyst is the most used method (Tan *et al*., 2019).

Although some biofuels are already represented in the world energy matrix by some developed and underdeveloped countries, there are still recent studies that evaluate viability and sustainability with diversified production processes and raw materials (Saladini *et al*., 2016). Brazil is among the largest producers and consumers of biodiesel in the world. According to the ANP statistical yearbook (ANP, 2018a), B100 biodiesel production in 2017 in the major regions and units of the Federation was 4,291,294 m^3. As of March 2018, the Brazilian government has enacted laws requiring the addition of 10% of biodiesel superimposed on mineral diesel for commercialization (B10) (ANP, 2018b).

Some factors contribute to the production of biodiesel in Brazil, such as the broad territory and technology for the planting of oleaginous raw materials such as soybean, canola, peanut, palm,

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castor bean, palm, macaúba, jatropha and others, slaughterhouses of animals that produce animal fats (Marcossi e Moreno-Perez, 2017). Soybean oil and bovine fat are the main raw materials used in Brazil.

In order to increase biodiesel production, research and technological innovations focus on the application of new methods of production involving raw materials such as microalgae and inedible and residual oils, aiming to reduce costs of current methods and avoid competition of raw material with too much products (food, cosmetics, pharmaceuticals, etc.) (Arumugam e Ponnusami, 2019; Sandouqa e Al Hamamre, 2019). One of the most important calls for biodiesel production from these new resources is that many of these crops will not displace the traditional areas of food crops, which is one of the main criticisms for the production of biodiesel from oleaginous plants (Atabani *et al.*, 2012; Tan *et al.*, 2019).

Residual frying oils are a problem for the environment, most of which are improperly disposed of, causing clogging in sewage pipes, river degradation, soil infertility, and in other ways contributing to increased pollution. With the evolution of environmental legislation, it is practically required that the oil be reused, for this reason, it becomes feasible to recycle residual frying oil due to the preservation of the environment. (Silva, 2013; Sabesp, 2008).

The continuous frying of food in vegetable oils leads to the formation of free fatty acids that alter the sensorial characteristics of the product and its physicochemical properties, the formation of free fatty acids causes chemical changes such as oxidation reactions, hydrolysis, and polymerization, besides physical changes such as smoke point reduction, browning, and foam and viscosity increase, rendering this matter inappropriate as an immediate reactant for transesterification reaction (Freire; Mancini-Filho; Ferreira, 2013). Neutralization processes, clarification, and drag evaporation are some methods used in oils to improve their quality as a raw material for biodiesel.

The quality control methods for waste oils and fats are complex and specific to determine each physical or chemical property. The acid index, peroxide index, and iodine index methods can be some methods that quickly and simply determine the amount of compounds formed during the oxidation. Gas chromatography, which determines which fraction of the oil has not undergone physical and chemical changes, is also highlighted, as well as determining which fractions concentrate the oxidized triglyceride degradation products, polymers, dimers, diglycerides, and free fatty acids. Other methods of quality control, such as Nuclear Magnetic Resonance (NMR), total polar compounds, fluorescence, or ultraviolet radiation, can also be used (Freire; Mancini-Filho; Ferreira, 2013).

Based on these factors, the purpose of this work is to obtain biodiesel (methyl esters) through the transesterification reaction of frying oil treated by the evaporation and entrainment method and to analyze the physicochemical properties and the conversion rate according to the norms standardization of ANP (2014), EN (2008), and ASTM (2005).

2 MATERIALS AND METHODS

2.1 Material

The municipal government of Jaguariaíva PR. provided the residual frying oil used for the treatment and for obtaining biodiesel from this study. The same was obtained from collection points of frying oil used by the population. The residual oil was filtered to remove solids and stored properly.

2.2 Oil treatment by evaporation and drag method

The treatment of the residual oil by evaporation and drag is due to adaptations of the methodology proposed by Watanabe *et al.* (2006). The evaporation and entrainment process was carried out for 15 minutes, and the treatment was carried out using a round bottom flask containing 100 mL of distilled water evaporated by a heating mantle. The flask was coupled with silicone hose in direct contact with 100 mL of frying residual oil. Subsequently, the oil was centrifuged and separated from the run-off water in a separatory funnel, and in the filtrate with anhydrous sodium sulfate (Synth).

2.3 Physicochemical characterization of residual oil

The Physicochemical characterization analyzes, such as moisture content, acidity index, saponification, iodine, and peroxide, were performed according to the methodology of the Adolfo Lutz Institute (IAL, 2008). The data obtained were interpreted by the method of analysis of variance, the means of the indices were compared using the Tukey test with 5% of probability. The pH was determined with the aid of a universal pH strip (pH-fix0-14).

2.4 The reaction of transesterification via homogeneous basic catalysis

The transesterification reaction was performed employing 100 mL of treated frying residual oil added in approximately 0.5 grams of NaOH P.A. (Dynamic, 98% concentration) dissolved in 50 mL of methyl alcohol P.A. (Dynamic). The reaction was carried out in a flat bottom flask coupled to the reflux condenser in a water bath at a temperature of 70 °C ± 5 °C, the reaction time of one hour and constant stirring. After the reaction, the phases of the products (biodiesel and glycerin) were separated through a separating funnel, where the corresponding phase of the biodiesel was washed with 0.1 mol L^{-1} HCl solution and distilled water, respectively, and then filtered with anhydrous sodium sulfate (Synth).

2.5 Conversion rate of methyl esters by ^{1}H NMR

The conversion rate of residual oil methyl esters was determined by ^{1}H NMR analysis of the residual oil before and after transesterification reaction. The analyses were performed on Agilent NMR spectrometer, Mercury Plus 300 MHz multinuclear model (Magneto NMR 300-OXFORD) under standard conditions for ^{1}H NMR using solvent $CDCl_3$ (Deuterated Chloroform).

The rate of conversion of triglycerides to biodiesel was determined using the method of Ruschel *et al.*, (2016), where the conversion rate was calculated using equation (Eq. 1) using the values of integral hydrogen spectra of the methylene group of carbon adjacent to the carbonyl (I-CH_2) and methoxy hydrogens of the O-CH_3 group.

$$C_{ME} = 100 \times \left(\frac{\frac{I_{ME}}{3}}{\frac{I_{\alpha-CH_2}}{2}} \right) \qquad \text{(Eq. 1)}$$

Where: C_{ME} = Conversion to methyl ester;

I_{ME} = Value of the methoxylic hydrogen spectrum (O-CH_3);

$I\alpha$-CH_2 = Value of the spectrum integral of the methylene hydrogens adjacent to the ester carbonyl.

3 RESULTS AND DISCUSSION:

3.1 Physicochemical properties of frying oil and biodiesel

In order to perform the transesterification reaction, it was necessary to analyze the physicochemical properties of the raw material with the purpose of informing the state of conservation of the oil before and after the treatment with evaporation and drag, and its sufficiency to obtain biodiesel by transesterification through homogeneous catalysis basic. The results obtained indicate the possibility and/or feasibility of improving the treatment method, adding other processes making the material propitious to reach higher conversion rates. (Silva, 2011; Völz, 2009). The results of the residual oil and biodiesel analyzes are shown in Tables 1 and 2.

According to Table 1, the results of the analyzes are outside the quality parameters of edible oils (ANVISA, 2006). The residual oil has a high acid value, probably predicted by the formation of free fatty acids due to oxidation and hydrolysis reactions when subjected to high temperatures. This is a detrimental factor to obtain biodiesel by transesterification through basic homogeneous catalysis, since it allows the formation of soaps, converting part of the raw material into salts of fatty acids (Ramos *et al.*, 2017; Silva, 2011). The effects of the steam drag process significantly reduced the acidity, but it remains high enough to apply the transesterification reaction, and the treatment method needs to be improved.

The iodine content of the treated oil has been supposedly reduced because lower halogenation reactions occur in double bonds of acidic compounds present in the oil, such as free fatty acids and others. The peroxide index is also probably lower due to the evaporation and drag process to remove partially compounds of oxidizing agents such as peroxides and hydroperoxides or other similar products from the raw material oxidized grease (Corsini e Jorge, 2006; Silva; Borges; Ferreira, 1999).

Pursuant to the ANP (DOU 26.8.2014), ASTM D6751 and EN 14214 standards for biodiesel standardization, the acid value for biodiesel shall be 0.50 mg KOH g $^{-1}$ and iodine maximum 120 g I_2/100 g according to EN 14111. There are no specifications for saponification index and also for peroxides, to analyze better the biofuel was replaced peroxide analysis by oxidation stability by induction period by the Rancimat method EN 14214 (Lôbo; Ferreira; Cruz, 2009) . The acidity index of biodiesel (1.14 ± 0.04 mg KOH g^{-1}) is higher than the quality standards, indicating that the steam drag treatment is inefficient to reduce acidic components in the residual oil to obtain biodiesel.

The biodiesel iodine content (101.50 ± 0.03 g I_2/100g) is within the quality standards, claiming that they have adequate unsaturation fatty acids in the biodiesel standard. The number of unsaturations in the biodiesel chain reflects on oxidative stability, pour point, fog, and cold clogging (Ramos *et al.*, 2017; Lôbo; Ferreira; Cruz, 2009).

The saponification index of treated waste oil and biodiesel is lower than the residual oil index, consistent results since, after treatment, they also have lower acidity indexes and moisture contents (Table 2) in their composition, requiring less demand for alkali needed for saponify the product in indirect titration.

The biodiesel obtained a peroxide index of 9.59 ± 0.03 mEq/kg, indicating that the initial oxidation state is relatively high and supposedly does not exceed 6 hours the induction time by the Rancimat method without addition of antioxidant. Silva *et al.* (2000) reported that both methods of analysis were based on biodiesel from frit residue residual oil (IP = 3.09 mEq/Kg and induction time of 8.19 hours) and ethanol (4.44 mEq/Kg, and induction time of 5.38 hours), concluding that the oxidative stability of biodiesel is inversely proportional to the peroxide index, that is, the higher the peroxide index the lower the oxidative stability.

Table 2. *Moisture content and pH of frying residual oil after treatment and biodiesel.*

Samples	Moisture content (%)	pH
Residual Oil	2.643^a (±0.030)	7.0
Filtered Oil	2.413^b (±0.015)	7.0
Treated Oil	0.733^c (±0.011)	8.0
Biodiesel	0.480^d (±0.003)	7.0

Table 2 shows that the treatment of the residual oil resulted in the increase of pH, favoring the production of biodiesel by transesterification through basic homogeneous catalysis and that after the transesterification reaction it became neutral (pH = 7.0). The moisture content of biodiesel of 0.480% corresponds to 480 mg/kg (0.0048 g), which is higher than the maximum amount allowed by law in biodiesel that is 200 mg/kg (0.0002 g), indicating that this method of biodiesel from waste oils reduces moisture, but in a non-effective way, being subject to microorganisms proliferation and corrosion during storage, storage and transport (Ramos *et al.*, 2017).

3.2 Conversion of triglycerides to methyl esters

In order to evaluate the rate of conversion of the transesterification reaction of the residual oil treated with the steam drag method, ^{1}H NMR analysis was carried out in the residual oil (Figure 1) to report through the spectra the components that characterize the triglycerides, and subsequently the types of hydrogens belonging to the different fatty acids.

The signals of the ^{1}H NMR spectra of Figure 1 are apparently similar to ^{1}H NMR spectra of soybean oil (Glycine max L.) (Shimamoto; Bianchessi; Tubino, 2019; Martin-Rubio; Sopelana; Guillén, 2018; Li *et al.*, 2018; Ruschel *et al.*, 2016), The results of this study indicate that a large part of its composition has triglycerides similar to those of refined soybean oil. The results obtained are similar to those of Wako *et al.*, (2018) which performed ^{1}H NMR analysis of residual oils, and determined the fatty acid profile by gas chromatography spectroscopy, stating that it had the same fatty acids found in soybean (oleic, linoleic, linolenic, palmitic, stearic, myristic, eicosanoic).

By analyzing ^1H NMR spectroscopy of the treated residual oil (Figure 1), the respective signals characterizing the triglycerides, the main components found in the residual frying oil, are noted: Sign "A" between 5.50-5.35 ppm represents hydrogen of the CH_2=CH_2 group, the "B" spectrum (5.35-5.25 ppm) glycerolic hydrogens of tertiary carb (H-CH), "C" groups (4.0-4.5 ppm) glycerol hydrogens of secondary carbon groups (H-CH_2), "D" (2.60-2.90 ppm) bis-allylic hydrogens (CH_2=CH-CH_2-CH=CH_2), "E" , (2.25-2.50 ppm) hydrogen of the methylene group of the carbon adjacent to carbonyl (Iα-CH2), "F" (1.80-2.20 ppm), allylic hydrogen, "G" (1.50-1.75 ppm) β-carbonyl hydrogen, "H" (1.25-1.50 ppm) hydrogens of H-CH_2 groups distant from CH_2=CH_2, groups, "I" (0.85-1.00 ppm) hydrogens of the H-CH_3 group of acids large and unsaturated fatty acids, and "J" (0.65-0.85 ppm) hydrogen peroxide from the H-CH_3 group (Martin-Rubio; Sopelana; Guillén, 2018; Popescu *et al.*, 2015).

Signals "B" and "C" in the ^1H NMR spectrum are specific to indicate whether triglycerides have reacted in the transesterification reaction. These signals are absent in the ^1H NMR spectra of biodiesel samples because in the conversion of oils to biodiesel no glycerol hydrogens are found in their composition. The disappearance of the signals "B" and "C" after the transesterification reaction theoretically justifies the conversion of biodiesel through the appearance of the new signal (K), a singlet located in the displacement 3.50-3.75 ppm corresponding to methoxylic hydrogels methyl group (COOCH3), as observed in Figure 2 (Ruschel *et al.*, 2016).

Figure 2 shows the 1H nuclear magnetic resonance spectrum, which corresponds to the biodiesel phase of the product of the transesterification reaction.

Observing the spectra in Figure 2, the presence of the "C" and "K" signals is noted, which proves that the triglycerides reacted with the methanol in the presence of the catalyst. However, the presence of the "C" signal shows that the product of the reaction did not reach 100% conversion, and may contain triglyceride residues such as diglycerides and/or monoglycerides, which have signals in the same spectral regions (4.10-4.30 ppm) than glycerol hydrogens (Ruschel *et al.*, 2016). These compounds affect changes in the physical and chemical properties of biodiesel carried out in this study, mainly in the acidity index.

The absence of the "B" signal is a predicted result, indicating that the tertiary carbon hydrogens do not makeup part of the biodiesel but of the glycerin, another product formed in the reaction.

To evaluate the conversion to esters by the calculation of equation 1 proposed by Ruschel *et al.*, (2016), the signal "K" was compared with the "E" signal (Iα-CH2), since this signal represents all the molecules and triglyceride derivatives such as diglycerides and monoglycerides, free fatty acids, and other long-chain carbon compounds, both of which may arise at the time of the reaction.

Table 3 shows the result of the conversion rate of methyl esters of biodiesel through the values of the integrals of the signals "E" and "K" applied in equation 1.

Table 3. Conversion of methyl esters and values integral's I_{ME} and $I\alpha\text{-}CH_2$.

Sample	**C_{ME} (%)**	**I_{ME}**	**$I\alpha\text{-}CH_2$**
Methyl esters	79.3	1.00	0.84

The result expressed in Table 1 shows that the transesterification reaction obtained a conversion rate of 79.3%, lower than 96.5%, which is the minimum established by ANP (2014), ASTM (2005), and EN (2008) for conversion to esters. In this paper, the low value of the conversion rate clarifies why the physical properties of biodiesel (Tables 1 and 2) have highly unsatisfactory results.

In this context, the product obtained from the reaction is prevented by law from being marketed because it is declared as a mixture of methyl esters instead of biodiesel.

4 CONCLUSIONS:

Regarding the main objective of this work, it was not possible to obtain biodiesel from frying oil treated by the steam and drag method, as a result of which the conversion rate in the methyl esters obtained is lower than 96.5% established by the quality parameters for biodiesel.

The effects of treatment of frying residual oil with the evaporation and entrainment process altered the physicochemical properties of the same, reducing the acidity, saponification, iodine, peroxide and the moisture content significantly, causing pH rise.

The conversion rate in esters of 79.3% is one of the factors for which the physical properties of the methyl esters obtained have values outside the quality standards for biodiesel in the index of acidity and moisture content. The high peroxide index indicates that the initial degree of oxidation is high, and probably antioxidant should be added to the methyl esters to reach the induction period of 6 hours, according to the parameters of quality for biodiesel.

5 ACKNOWLEDGMENTS:

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Table 1. Acidity, saponification, iodine, and peroxide indexes of frying residual oil after treatment and biodiesel.

Samples	**Indexes**			
	Acidity (mg KOH g^{-1})	**Saponification (mg KOH g^{-1})**	**Iodine (g I_2/100g)**	**Peroxide (mEq/kg)**
Residual Oil	9.36^{ab} (±0.04)	223.83^{a} (±0.08)	114.24^{ab} (±0.06)	19.33^{a} (±0.06)
Filtered Oil	9.35^{ab} (±0.02)	223.04^{b} (±0.10)	114.18^{ab} (±0.08)	19.17^{b} (±0.05)
Treated Oil	7.85^{c} (±0.02)	178.38^{c} (±0.04)	101.52^{c} (±0.07)	14.46^{c} (±0.03)
Biodiesel	1.14^{d} (±0.04)	163.12^{d} (±0.05)	101.50^{d} (±0.03)	9.59^{d} (±0.03)

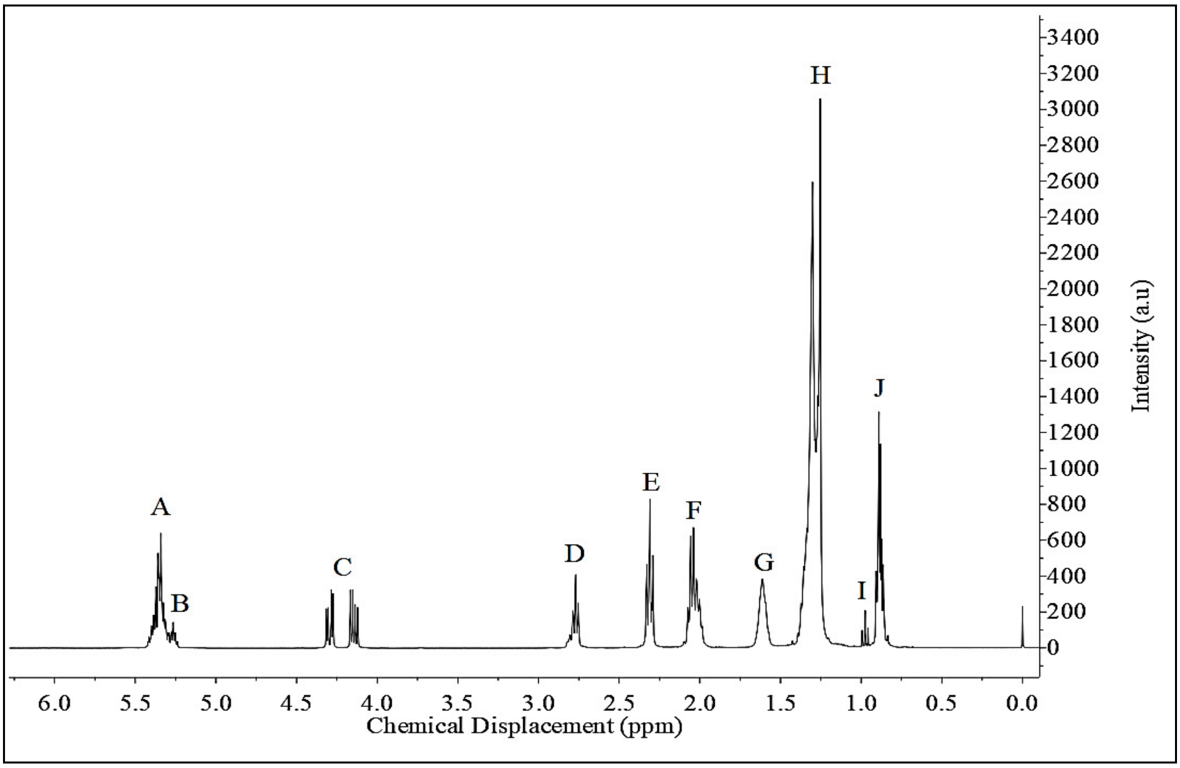

Figure 1. *^{1}H NMR spectra of residual frying oil treated by stream drag method.*

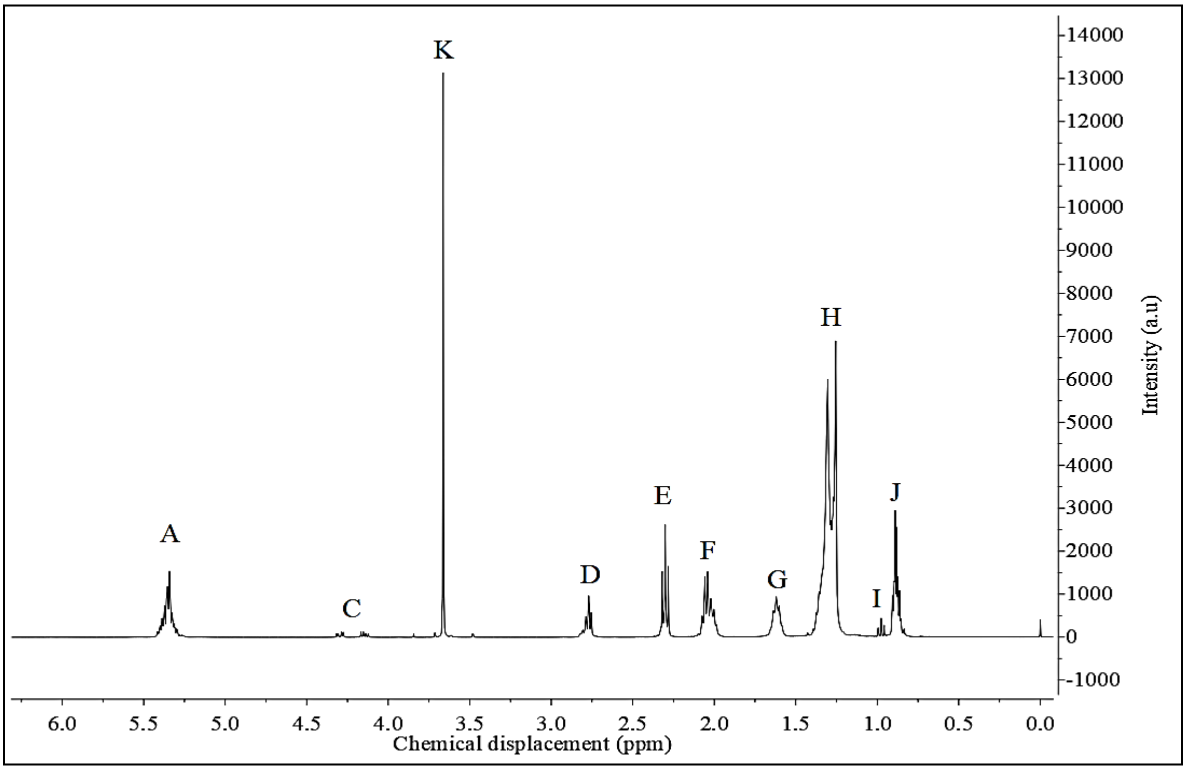

Figure 2. *^1H NMR spectra of biodiesel from frying residual oil*

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Introduction: The introduction must clearly state the problem, the reason for doing the work, the hypotheses or theoretical predictions under consideration, and the essential background. It should not contain equations or mathematical notation. A brief survey of the relevant literature so that a non-specialist reader could understand the significance of the presented results.

Materials and Methods: Provide sufficient details to permit repetition of the experimental work. The technical description of methods should be given when such methods are new.

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1. Varma, R. S.; Singh, A. P.; J. Indian Chem. Soc., 1990, 67, 518.

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2. Provstyanoi, M. V.; Logachev, E. V.; Kochergin, P. M.; Beilis, Y. I.; Izv. Vyssh. Uchebn. Zadev.; Khim. Khim. Tekhnol. 1976, 19, 708. (CA 85:78051s).

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3. Vidotti, M.; Silva, M. R.; Salvador, R. P.; de Torresi, S. I. C.; Dall'Antonia, L. H.; Electrochimica Acta (2007), doi:10.1016/j.electacta.2007.11.029.

It is recommended to give composite references instead of a list of separate references. The style of composite references is as follows:

4. Varela, H.; Torresi, R. M.; J. Electrochem. Soc. 2000, 147, 665; Lemos, T. L. G.; Andrade, C. H. S.; Guimarães, A. M.; Wolter-Filho, W.; Braz-Filho, R.; J. Braz. Chem. Soc., 1996, 7, 123; Ângelo, A. C. D.; de Souza, A.; Morgon, N. H.; Sambrano, J. R.; Quim. Nova 2001, 24, 473.

Patents

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5. Hashiba, I.; Ando, Y.; Kawakami, I.; Sakota, R.; Nagano, K.; Mori, T.; Jpn. Kokai Tokkyo Koho 79 73,771 1979. (CA 91:P193174v)

6. Kadin, S.B.; US Pat. 4,730,004 1988. (CA 110:P23729y)

7. Eberlin, M. N.; Mendes, M. A.; Sparrapan, R.; Kotiaho, T. Br PI 9.604.468-3, 1999.

Books

With editors

8. Regitz, M. Multiple Bonds and Low Coordination in Phosphorus Chemistry; Regitz, M.; Scherer, O. J., eds.; Georg Thieme Verlag: Stuttgart, 1990, cap. 2.

Without editors

9. Cotton, F.A.: Wilkinson, G.; Advanced Inorganic Chemistry, 5th ed., Wiley: New York, 1988.

Computer programs (software)

10. Sheldrick, G. M.; SHELXL-93; Program for Crystal Structure Refinement; University of Gottingen, Germany, 1993.

Theses

11. Velandia, J. R.; Ph.D. thesis, Federal Rural University of Rio de Janeiro, Brazil, 1997.

Presentations at meetings

12. Ferreira, A. B; Brito, S. L.; Abstracts, 20th Annual Meeting of the Brazilian Chemical Society, Poços de Caldas, Brazil, 1998.

Internet pages

13. http://www.sbq.org.br/jbcs, accessed June 2001. (minimal of information requested)

Unpublished material

For articles accepted for publication: Magalhães, U. H.; J. Braz. Chem. Soc., in press.

For articles submitted but not yet accepted: Magalhães, U. H.; J. Braz. Chem. Soc., submitted.

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