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PRELIMINARY STUDY FOR OBTAINING BIOFUELS FROM AQUATIC PLANTS

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Abstract. *Biomass plays an important role due to its abundant availability, as well as being completely renewable and presented low cost. The liquefaction process consists of transforming the biomass in the form of large and small solids into bio-oil that can be used as a liquid biofuel. The excessive increase in aquatic plants impairs the energy generation in hydroelectric plants, since their accumulation in the grids leads to a decrease in water intake through the turbine as well as to a greater pressure on the grates, which may deform or break them, making the generation unit's operation unavoidable. Thus, the present work aims to study the conditions to be adopted in order to carry out the liquefaction process via solvolysis of the invasive aquatic plant Egeria densa. It was found that the highest yield was obtained when the reaction medium was stirred for 60 minutes at 130 ° C. For a constant temperature the increase in the reaction time causes an increase in the liquefaction yield and for the constant reaction time an increase in the temperature leads to an increase in the liquefaction yield. In general, the results indicate that it is feasible to use Egeria densa for bio-oil production.*

Keywords: *Biofuel, liquefaction, biomass, aquatic plants*

1. INTRODUCTION

Among the several types of renewable energy, biomass energy presents itself as a promising substitute for fossil raw materials for the sustainable production of fuels and chemical products, presenting as an advantage of its low cost, as well as being considered a renewable natural resource, thus contributing to a reduction of environmental impact. The use of biomass in the biofuels production has the potential to supply 30% of the global demand for these materials.

In order to use the biomass as a source for electricity generation, heat supply and fuel for automobiles, it must be converted into solid, liquid or gaseous fuels. Over the past decades, several conversion techniques have been developed to provide liquid products from different types of biomasses for use as fuels and chemicals products.

Among the various techniques, direct liquefaction is one of the most promising routes for liquid fuels production using biomass with high moisture content, since in this technique water serves both as a reaction medium and as a reagent.

In the liquefaction process, initially the macromolecules contained in the biomass (lipids, proteins and carbohydrates) are depolymerized into simpler molecules in the presence of a suitable catalyst and then the unstable fractions of the compounds are repolymerized to form bio-oil with a wide range of molecular distribution. Changes during the process involve several types of reactions such as solvolysis, depolymerization, decarboxylation, hydrogenolysis, hydrogenation, among others (Demirbas, 2000).

According Fan *et. al.*, 2011, among the thermal liquefaction conversion methods, solvolysis is the most widely used method because the process temperature is relatively lower compared to the pyrolysis process temperature, preventing the formation of tar compounds due to cross-linking between hydrocarbons and aromatic compounds (Liu and Zhang, 2008).

The technique consists of dissolving the biomass in reactive organic solvents such as phenol, polyhydric alcohols, ethylene carbonate, among others. This technique uses moderate temperatures (100 to 250ºC), which may or may not be used as a catalyst. In the solvolysis process, biomass is depolymerized in the presence of organic reagents to form liquid biofuels and useful chemicals (Lin *et al*., 2004). This technique has been shown to be very attractive given that high pressures or drying processes are not necessary, being carried out at moderate temperatures.

For the solvolysis process, the conversion of biomass into a liquid product occurs through a complex sequence of steps involving changes in physical structure and chemical bonds (Barbary, 2007). The mechanism of this type of reaction initially involves the creation of a cellular structure via solvolysis, with consequent depolymerization of the solubilized molecules. Then, thermal decomposition occurs where new molecular rearrangements will be originated through dehydration, decarboxylation, breaks in C-O and C-C bonds (Hu and Li, 2014). The formed compounds are then rearranged through condensation, cyclization and polymerization reactions, giving rise to new compounds (Barbary, 2007).

Aquatic plants play an extremely relevant role in water systems, as they are directly related to the energy and carbon stock at the bases of food pyramids, thus promoting suitable habitats for various organisms (Neves, 2002). However, the excessive increase in these aquatic plants impairs the use of water bodies, both from an environmental point of view and for human use, also causing problems related to navigation as well as the generation of energy in hydroelectric plants, the capture of water for irrigation and consumption (Pitelli, 1998).

Among the numerous sources of renewable energy, aquatic biomass remains virtually unexplored, including macrophyte plants. Aquatic plants can be converted into various energy sources through different processes. Thus, there are still several lines of research to be explored for the use of aquatic plants using different conversion techniques, such as fermentation (Mishima *et al*., 2007; Huesemann *et al*., 2018), hydrothermal liquefaction (Neveux *et al.*, 2014; Ong *et al*., 2019; Kumar *et al*., 2019), pyrolysis (Miranda *et al*., 2014; Carregosa, 2016; Santos *et al*., 2018).

Since there are no studies in the literature referring to the use of macrophyte plants for the liquefaction process via solvolysis, the present work aims to carry out an exploratory pre-study of the conditions to be adopted so that the macrophyte Egeria densa liquefaction process can be carried out. In the study, different reaction times and different temperatures were adopted in order to determine the possible conditions to explore the liquefaction process of submerged aquatic plants for the production of liquid biofuels.

2. METHODOLOGY

2.1 Materials

Egeria densa was collected from the Paranapanema River in Rosana/SP (Figure 1). The plants were cleaned thoroughly with tap water to remove adhering materials and mud, cut into pieces smaller, 1–2 cm length, drained and remained for a period of 24 hours at room temperature before being used for liquefaction (Figure 2).

2-Ethylhexanol (2HE) and Diethylene glycol (DEG) were used as the liquefaction reagents. P-toluenesulfonic acid was used as the acidic catalyst.

Figure 1. Collection of Egeria densa plants.

Figure 2. Egeria densa clean and fresh and cut and dried, respectively.

2.2 Proximate analysis

The proximate analysis was done as per methodology described in ASTM (E-870-82) for biomass and waste. Were determined the ash%, moisture%, volatile matter% and fixed carbon% for the fresh plants and for the plants that remained 24 hours at room temperature.

For moisture content, Dense Egeria was kept in crucible and heated at 110ºC for two hours in the hot air oven and moisture (M) was calculated using Equation (1):

$$M[\%] = \left(\frac{Initial\ weight - Final\ weight}{Initial\ weight}\right) \times 100, \tag{1}$$

For ash content, the sample was ignited at 750 ºC for 2 hours in a muffle furnace. The ash content was calculated in material using Equation (2):

$$Ash\ (\%) = \left(\frac{Initial\ weight\ -\ Final\ weight}{Initial\ weight}\right) \times\ 100, \tag{2}$$

Then the sample was ignited in a muffle furnace at 850 ºC ± 20 ºC for 6 min and volatile matter (VM) was calculated using the Equation (3):

$$VM(\%)\ =\ (\%loss\ in\ weight\ -\ \%\ moisture\ ) \times 100, \tag{3}$$

To determine the fixed carbons (FC) Equation (4) was used:

$$FC(\%)\ =\ 100\ -\ (\%M\ +\ \%VM\ +\ \%Ash) \tag{4}$$

All measurements were repeated in triplicate and a mean value is reported.

2.3 Liquefaction process

The liquefaction was carried out in a three-neck flask (500 ml) equipped with a heated magnetic stirrer, reflux condenser and thermometer. Liquefying solvents and acidic catalyst were added to the flask reactor. The flask was immersed in an oil bath and preheated at a set temperature. The experimental bench developed to carry out the liquefaction tests is shown in Figure3.

Figure 3. Liquefaction experimental bench.

To carry out the liquefaction tests, the macrophyte Egeria dense was used, the stipulated solvent mass ratio was 1:3 (DEG:2EH) and the catalyst used was 3% of the total biomass weight (biomass, DEG and 2EH). Table 1 shows the experimental conditions adopted in this study.

Table 1. Experimental conditions.

Test	Time reaction (min)	Temperature (ºC)
1	20	100
2	40	100
3	60	100
4	20	110
5	40	110
6	60	110
7	20	120
8	40	120
9	60	120
10	20	130
11	40	130
12	60	130

Initially, silicone oil was introduced into the container where the reactor will be placed up to a certain level so that the reaction mixture is always in contact with the oil, taking care that it does not overflow. This container was placed under a stirring and heating plate and a thermometer was used to monitor the temperature in the thermal bath. When the temperature of liquefying chemicals reached the maximal value (100, 110, 120 and 130 ºC), a specific quantity of dry Egeria densa was added gradually. Then, the Diethylene glycol (DEG) was added to the rector, followed by 2-Ethylhexanol (2EH) and the acid catalyst that was diluted in the solution.

The mixture was continuously stirred during the liquefaction process to obtain homogeneously liquefied product for a specified time. After the reaction, the heating was turned off and the reaction mixture was cooled until the temperature inside the flask decreased by approximately 20°C, keeping on the agitation. The liquefaction experiments were performed under different reaction temperature (100, 110, 120 and 130 ºC), retention time (20, 40 and 60 min).

The extent of liquefaction reaction was gravimetrically evaluated on the basis of the residue content (unreacted raw material). The liquid products (LR) and solid residue (SR) were separated by filtration under vacuum through a pre-weighted filter paper (Figure 4).

Figure 4. Filtering process.

The SR was washed with 100% acetone and dried in oven at 105 ºC for 24 h and then weighed to calculate the liquefaction yield.

The liquefaction yield (LY) was calculated with the Equation (5):

$$Liquid\ yield\ (\%) = \left(1 - {Dry\ weight\ of\ solid\ residue}/{Dry\ weight\ of\ Egeria\ densa}\right) \times 100 \tag{5}$$

3. RESULTS AND DISCUSSION

3.1 Proximate analysis results

The proximate analysis is very important, once allows determine the thermal characteristic of a feedstock to be used for biofuel production.

The results obtained for the determination of moisture were made considering two scenarios. Initially, in natura Egeria densa was used, only passing through a process of separating unwanted waste such as stones, sand and mussels. Then, biomass storage was considered, where the plants after being removed from the water was separated, washed, drained and remained for a period of 24 hours at room temperature.

Fresh plants presented an average moisture of 91.8% ±0.02 while dry plants presented 73.6% ±0.19, of average moisture, so there was a reduction of 18% in relation to the in natura test.

The results of proximate analysis obtained for Egeria densa that will be used in liquefaction process were: moisture, 73.6%±0.19; ash, 4.55%±0.04; VM, 69.66%±0.09 and FC, 36.33%±0.30.

3.2 Effect of temperature on the liquefaction

Figure 5 showed the effect of reaction temperature on the liquefaction yield. The samples evaluation was obtained for liquefaction solvent, DEG/2EH=1/3; biomass loading, 20%; catalyst loading, 3% and 20 min of reaction.

It is verified that the liquefaction yield increased as the liquefaction temperature increased from 100 to 130 ºC, so that the liquefaction effect is improved as the reaction temperature increases. The liquefaction yield reached 7.74%, 16.41%, 28.58 and 31.50% for 100, 110, 120 and 130 ºC, respectively.

During the liquefaction process, the degradation and re-polymerization between the liquefied products occurred simultaneously, being the temperature an important parameter. Degradation converts biomass into low molecular weight molecules and reduces the residue fraction, increasing the yield, on the other hand, re-polymerization of the liquefied product produces insoluble macromolecules and increases the residue fraction, decreasing the yield.

From the results obtained, when the reaction temperature increases from 100 to 130 ºC the degradation was predominant in the Egeria densa liquefaction, improving the liquefaction effect.

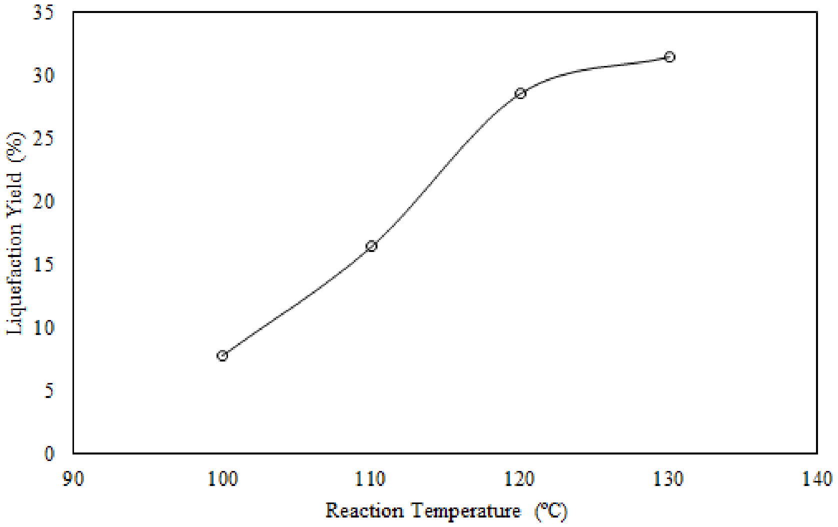

Figure 5. Effect of temperature on the liquefaction. Reaction conditions: time, 20 min; liquefaction solvent, DEG/2EH=1/3; biomass loading, 20%; catalyst loading, 3%.

3.3 Effect of reaction time on the liquefaction

Figure 6 presents the effect of the reaction time on the liquefaction yield for samples produced under the following liquefaction conditions: liquefaction solvent, DEG/2EH=1/3; biomass loading, 20%; catalyst loading, 3% and reaction temperature of 120 ◦C.

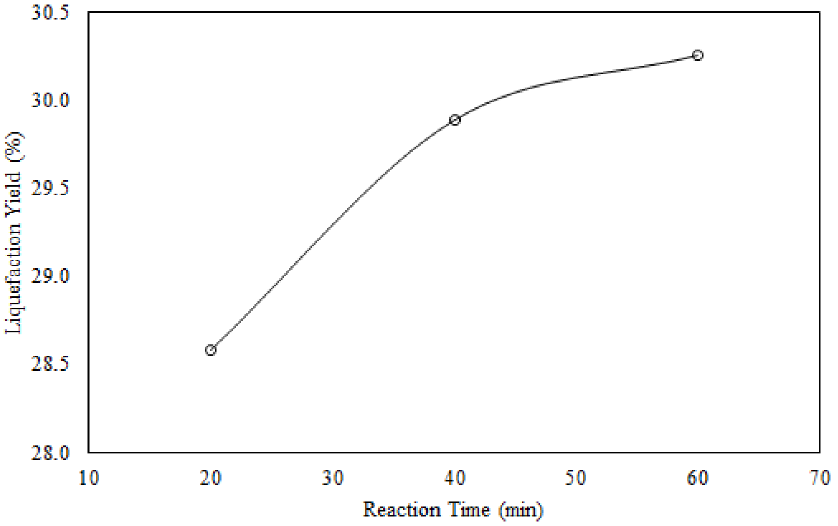

Figure 6. Effect of reaction time on the liquefaction. Reaction conditions: reaction temperature, 120 ºC; liquefaction solvent, DEG/2EH=1/3; biomass loading, 20%; catalyst loading, 3%.

The liquefied Egeria densa reached a yield of 28.58%, 29.89% and 30.26% for 20, 4 and 60 min, respectively, therefore, the liquefaction effect is improved as the reaction time increases. Such behavior can be attributed to the fact that Egeria densa compounds were decomposed and depolymerized to small molecules.

3.4 Liquefaction tests

After finishing the reaction time, the mixture showed a pasty appearance of dark green color as can be seen in Figure 7, and the contents of the reaction balloon go through the filtering process (Figure 8).

Figure 7. Mixture after reaction time.

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Figure 8. Filtering of the mixture obtained in the liquefaction process.

Figure 9 shows the residue obtained after liquefaction and the liquefied of Egeria densa.

Figure 9. Residue obtained after liquefaction and the liquefied.

After finishing the washing, the residue that remained on the filter paper goes to the oven together with the clock glass for 24 hours, to determine the efficiency of the process.

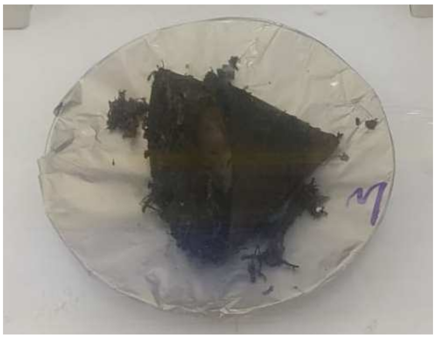

Figure 10. Dry residue

The liquefaction yield obtained for each experimental condition are shown in Figure 7. For all the reactions conditions, it is verified that the highest yield, approximately 39%, was obtained when the mixture was stirred for 60 minutes at 130°C.

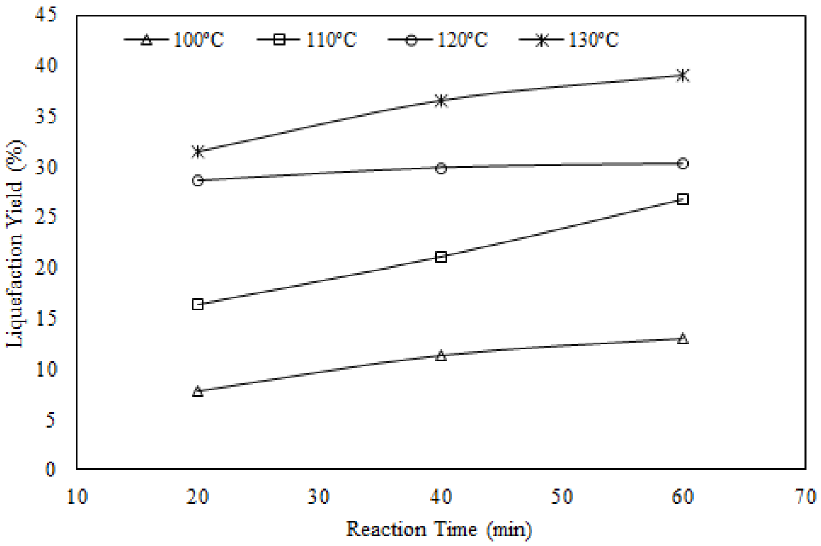

Figure 5. Liquefaction yields.

It is verified that for all the experimental conditions analyzed the increase in the reaction temperature as well as the increase in the reaction time leads to an increase in the liquefaction yield. For all the conditions the increase in liquefaction yields can be attributed to the degradation process that converts biomass into low molecular weight molecules and reduces the residue fraction, conducing to an increasing the yield.

4. CONCLUSIONS

In the present work, tests were carried out that made it possible to understand the liquefaction process of macrophyte plants, especially Egerea Densa.

In the moisture tests it was possible to determine the high water content present in this type of biomass and how the climate can affect its moisture content. Thus, it is understood that for large-scale production, in hydroelectric plants with algae removed from the protection grids of the turbines and the dam, the storage time can change its moisture, requiring a new relationship between biomass mass, quantity of reagents and reactor temperature, as the longer they are stored, the lower their humidity.

For all experimental conditions of the liquefaction tests, the increase in the reaction temperature and the increase in the reaction time leads to an increase in the liquefaction yield. Under all conditions, the increase in liquefaction yields can be attributed to the degradation process that converts biomass into low molecular weight molecules and reduces the waste fraction, leading to an increase in yield.

The results obtained so far are satisfactory and indicate that it is feasible to use submerged aquatic plants, especially Egerea Densa. In the tests carried out it was possible to obtain liquefied, however, as they are preliminary tests, the yields obtained were low, this fact can be attributed to the lower temperatures used in the experiment due to the limitation of the available heating system. Thus, in order to increase the liquefaction yields, longer reaction times as well as higher temperatures in the reaction medium will be analyzed in future works.

5. ACKNOWLEDGEMENTS

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