

## LIQUEFACTION OF PALM OIL FIBER (*Elaeis* sp.) IN SUPERCRITICAL ETHANOL

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**Abstract.** In the present work thermoliquefaction of palm fiber for bio-oil production was investigated by using supercritical ethanol. For this, a bench-scale experimental apparatus in a semi-continuous mode was developed. Experimental runs were carried out in a tubular reactor (10 mL) at pressure and solvent flow rate of 150 bar and 1 mL.min<sup>-1</sup>, respectively. The effect of temperature (300, 400 and 500°C), heating rate (10 and 30°C.min<sup>-1</sup>) and cracking time (10 and 30 min) on the biomass conversion into bio-oil and chemical profile of the bio-oil was investigated. The biomass conversion of the thermoliquefaction process changed from 83 to 95% with a bio-oil yield between 56 and 87% depending on the experimental conditions. Generally, a temperature rise led to an increase on the bio-oil content and a decrease in the gas and char content. Increasing the heating rate led to a decrease in bio-oil yield with increase in the char produced. The variation of the cracking time did not present a definite effect regarding the biomass conversion. Water content of the bio-oil was below 1%. The characterization of the bio-oil chemical profile was made by gas chromatography with mass spectrometry (GC-MS). It was found that the chemical profile of the bio-oil is tightly dependent on the thermoliquefaction temperature. At 300 °C mainly sugars were generated whereas at 400 °C alcohols were the main compounds identified and at 500 °C the main compounds were phenols. Chromatography also revealed that the bio-oil presents low acid percentage indicating that supercritical ethanol esterified the acids generated during the thermocracking.

**Keyword:** Liquefaction, supercritical ethanol, bio oil, oil palm fiber

### 1. Introduction

The need for new renewable energy sources regarding of the high demand for fossil fuels, make biomass very attractive due to its high energetic potential [1,2]. Several researches are in development in the world with the aim of defining the more satisfactory utilization of the several biomass wastes. The Brazilian biodiversity presents regional characteristics providing an excellent means to the development of study in this sense [3].

A crop that stands out in Brazil is the palm culture (*Elaeis* sp.). Palm oil offers two types of oil, the palm oil which is extracted from fiber, which is mainly used for food, and palm kernel oil that is extracted from endosperm, mainly used in pharmaceutical industry. Brazil produced in 2009 more than 1 million tons of palm fruits, mainly in the states of Pará and Bahia generating large amounts of lignocellulosic wastes, such as fiber mesocarp, exocarp, palm kernel cake and empty fruit bunches by the palm oil processing [4,5].

The physical and chemical properties are different for each biomass type and, directly influence the properties and distribution of the compounds generated. Each lignocellulosic waste displays a particular characteristic when cracked, due to the different proportions of the cellulose, hemicelluloses and lignin present into biomass [6]. The proportion of these compounds in palm fiber reported in the literature are about 51wt% cellulose, 23 wt% hemicelluloses and about 15% lignin [7].

These lignocellulosic wastes can be converted into bio-oil by a thermoconversion process. The bio-oil generated by pyrolysis process is a complex mixture of organic compounds, chemically and thermally unstable with a high amount of water and acids [8]. The use of supercritical solvents in the biomass thermoconversion, namely thermoliquefaction, produces a more stable bio-oil with better properties, since the solvent acts as a hydrogen donor stabilizing fragments. Examples of solvents are water, acetone, ethanol and methanol or mixtures of these [7,9,10]. Utilization of alcohols as solvents also provides the formation of esters by esterification/transesterification of the acids and residual oil present in the biomass, therefore obtaining higher yields compared to conventional pyrolysis process [11,12]. In this sense, the objective of this work was the thermoliquefaction of palm fiber at high pressure and temperature using supercritical ethanol as solvent aiming the production of a high quality bio-oil with low water and acid content.

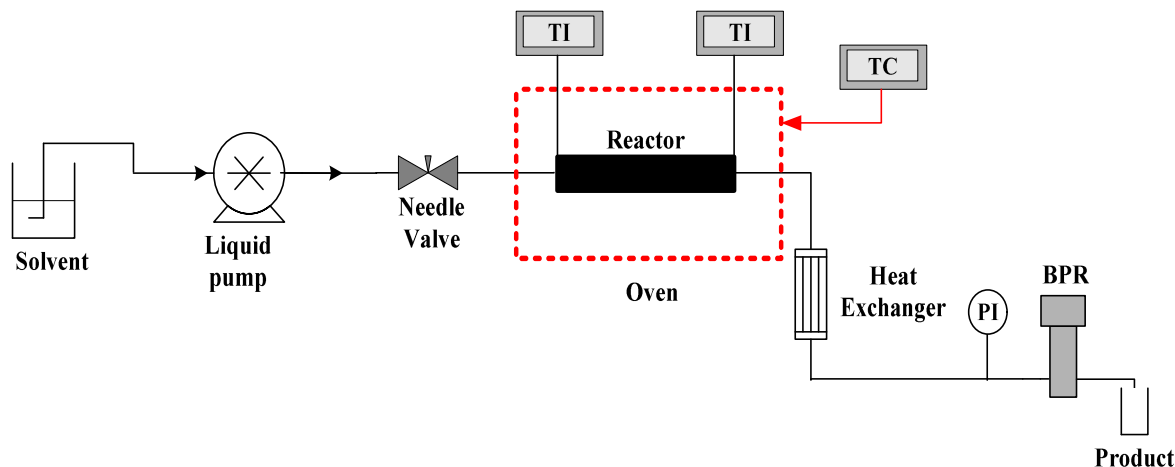
## 2. Materials and Methodology

### 2.1 Biomass Processing

The palm fiber employed in the thermoliquefaction experiments by using ethanol (VETEC, 99% purity) was obtained after pulping and oil extraction of the palm fruit (kindly supplied by the Empresa Baiana de Desenvolvimento Agrícola, EBDA, located in the state of Bahia, Brazil). After drying (60 °C, 24 h) and oil extraction with hexane, according to AOAC norm [13], the palm fiber was classified according to mean particle size (about 5 mm) to be used in the thermoliquefaction process. As the oil content of the palm fiber is not the objective of this work, this content was not determined. After fiber pre-treatment, its water content was measured by Karl Fischer titration (Metrom, 870 KF titrino plus).

### 2.2 Thermoliquefaction Apparatus and Procedure

All experiments of thermoliquefaction using supercritical ethanol were conducted in a semi continuous bench scale unity. The schematic diagram of the experimental apparatus is presented in Figure 1.



**Figure 1.** Experimental apparatus for biomass thermoliquefaction. (TI) Temperature indication; (TC) temperature control; (PI) pressure indication; (BPR) back pressure regulator.

The experimental apparatus for biomass thermoliquefaction using ethanol as solvent consists mainly of an oven with electrical resistances (JUNG, Model 2310) equipped with a PID temperature controller (NOVUS, Model N1100) that allow the heating inside the oven at different heating rates. A stainless steel tube with 3/8" external diameter with 30 cm length and 10 mL volume was used as reactor. A digital HPLC liquid pump (Fischer Scientific, Acuflow Series III) was used for solvent pumping. The unit also included a heat exchanger to cool the product that exits the furnace. A back pressure regulator (BPR) (Swagelok, KHB series, model 1W0A4C6P60000) was used to pressure control in the entire system. A pressure transducer (NOVUS, model TP-691 Huba Control) is placed before the BPR for pressure monitoring. Two type K temperature

sensors were inserted at the reactor inlet and outlet and connected to universal process indicators (NOVUS, model N1500). A needle valve (HIP, model 1511AF1) was placed between the HPLC pump and the oven to isolate the unit and the pump as necessary.

For thermoliquefaction reactions ethanol was used as hydrogen donor and sterifying agent with the aim of solubilize and stabilize the fragments generated in the fiber cracking. The pressure of the system and the ethanol flow rate were maintained at 150 bar and 1 mL.min<sup>-1</sup>, respectively. According to Akhtar and Amin [12], high density medium results in enhanced biomass decomposition and product extraction. However, once supercritical conditions for liquefaction are achieved, pressure has little or negligible influence on yield of liquid oil. Also, according to these authors, small residence times are usually preferred because they produce more amount of oil. The liquefaction temperatures investigated were 300, 400 and 500 °C, heating rates of 10, 20 and 30 °C/min and cracking times of 10 and 30 min.

The experimental procedure started with loading approximately 0.8 g of the palm fiber to the reactor and then this is inserted into the oven and connected to the system. All system is then filled with solvent through the HPLC pump at a flow rate of 0.2 mL.min<sup>-1</sup>. The system was pressurized by the BPR manipulation at constant flow rate and the pressure monitored by the pressure transducer. After pressure was reached the constant value, the system was heated at specified heating rate up to the desired temperature and then, was maintained at these conditions for 10 or 30 minutes, maintaining the flow rate at 0.2 mL.min<sup>-1</sup>. After this time, the flow rate was increased to 1 mL.min<sup>-1</sup> and the product generated during the liquefaction process, after cooling, was collected in screw cap bottles during 1h. After each experimental run the char was recovered and weighted to determine the liquefaction conversion.

The samples of liquefaction experiments were dried at 60 °C until no weight difference was observed. The bio-oil yield was measured as the percentage of mass ratio between bio-oil and palm fiber charged into the reactor. The quantification of the gas generated was made by the difference between the liquefaction yield and the bio-oil yield.

### **2.3 Chromatographic analysis**

The GC-MS analysis was carried out using a QP 2010-Plus GC-MS spectrometer (Shimadzu) with a capillary column, DB-5 (5% phenyl, 95% dimethylpolysiloxane) (30 m x 0,25 µm x 0,25mm). The flow rate of carrier gas He was 1 mL.min<sup>-1</sup> and the split ratio of 1:30. The oven program was 4 min isothermal at 60 °C, then 5 °C.min<sup>-1</sup> to 290 °C and finally 25 min at 290 °C. The injector temperature was 280°C and ion source was 250 °C.

## **3. Results and discussion**

### **3.1 Thermoliquefaction using Supercritical Ethanol**

The effect of temperature (300 - 500°C), heating rate (10 and 30°C.min<sup>-1</sup>) and cracking time (10 and 30 min) on the thermoliquefaction of palm fiber using supercritical ethanol was investigated. Pressure and solvent flow rate were maintained at a constant value of 150 bar and 1 mL.min<sup>-1</sup>. The experimental conditions and the results of products yield (bio-oil, char and gas) are presented in Table 1. Some experimental conditions of liquefaction (1, 5, 9, 12 and 13) were duplicated to determine the experimental uncertainty. The water content was measured and it was found to be less than 1 wt%.

According to results presented in Table 1 and depicted in Figure 2, it is possible to observe that the oil yield varied from 56.3 to 87.2% depending of the experimental conditions. The char yield was low, ranging between 5.6 and 16.5%, while the gas yield varied from 5.8% to 27.2%.

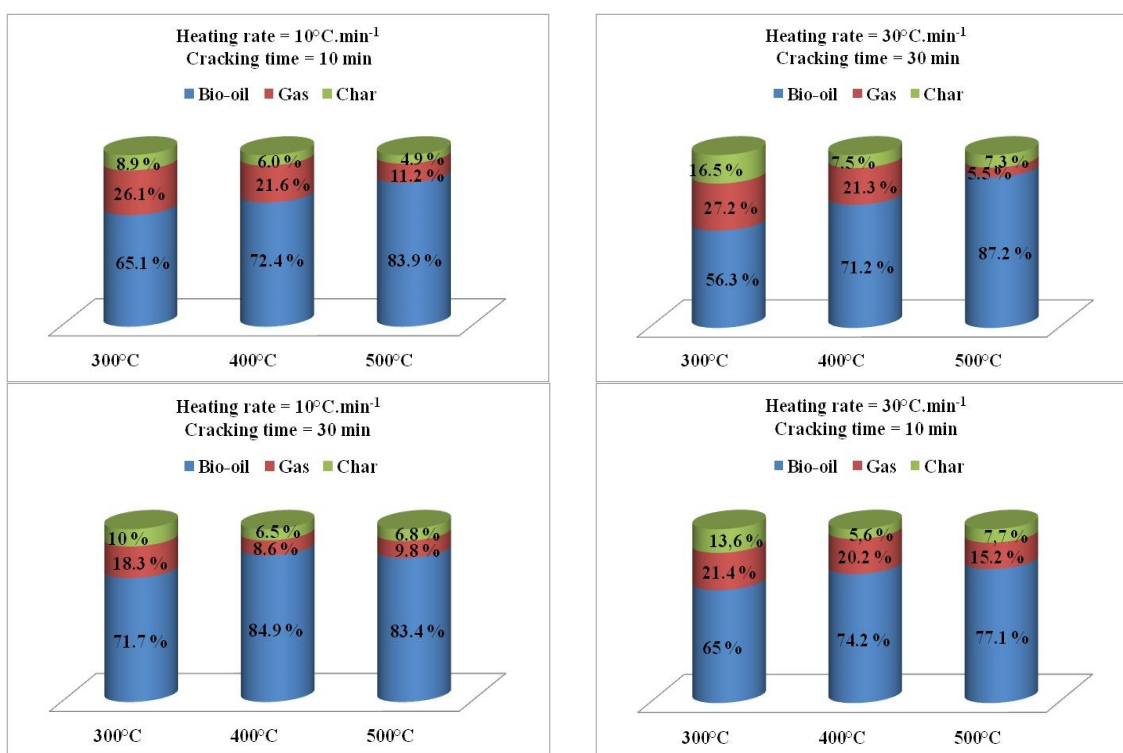
Generally, by increasing the temperature it was possible to increase the conversion into bio-oil fraction, while the increase of the heating rate decreased the bio-oil conversion and increased the char formation. The variation in the cracking time did not show a definite effect into product formation.

The lowest bio-oil conversions (56.3%) were obtained at 300 °C with the highest char (16.5%) and gas (27.2%) production. When the experiments were conducted at 400 °C there was an effective increase in bio-oil conversion with a consequent decrease in char and gas production. For a heating rate of 10 °C.min<sup>-1</sup> the mean yield in bio-oil was 76.6% whereas for the heating rate of 30 °C.min<sup>-1</sup> the mean yield was 72.7 %. For temperature of 500 °C the higher yield of bio-oil was obtained at a heating rate of 10 °C.min<sup>-1</sup> (83.6%) while at the higher heating rate the bio-oil yield was decreased (79.3%).

**Table 1.** Experimental conditions and results of palm fiber thermoliquefaction using supercritical ethanol in a semi-continuous process.

Run	HR (°C.min <sup>-1</sup> )	CT (min)	T (°C)	Bio-oil (%)	Gas (%)	Char (%)
1	10	10	300	65.1 ±0,7	26.1 ±1.4	8.9 ±1.1
2	10	10	400	72.4	21.6	6.0
3	10	10	500	83.9	11.2	4.9
4	10	30	300	71.7	18.3	10.0
5	10	30	400	80.9 ±5,6	12.8 ±6.0	6.2 ±0.3
6	10	30	500	83.4	9.8	6.8
7	30	10	300	65.0	21.4	13.6
8	30	10	400	74.2	20.2	5.6
9	30	10	500	78.6 ±2,1	12.0 ±4.6	9.5 ±2.5
10	30	30	300	56.3	27.2	16.5
11	30	30	400	71.2	21.3	7.5
12	30	30	500	80.0 ±10,1	12.5 ±10.0	7.3 ±0.1
13	20	20	400	87.2 ±1.2	5.8 ±0.2	7.1 ±1.0

HR = Heating Rate; CT = Cracking Time; T = Temperature.



**Figure 2.** Effect of process variables on the bio-oil, char and gas yield for thermoliquefaction of palm fiber using supercritical ethanol at 150 bar and 1 mL.min<sup>-1</sup>.

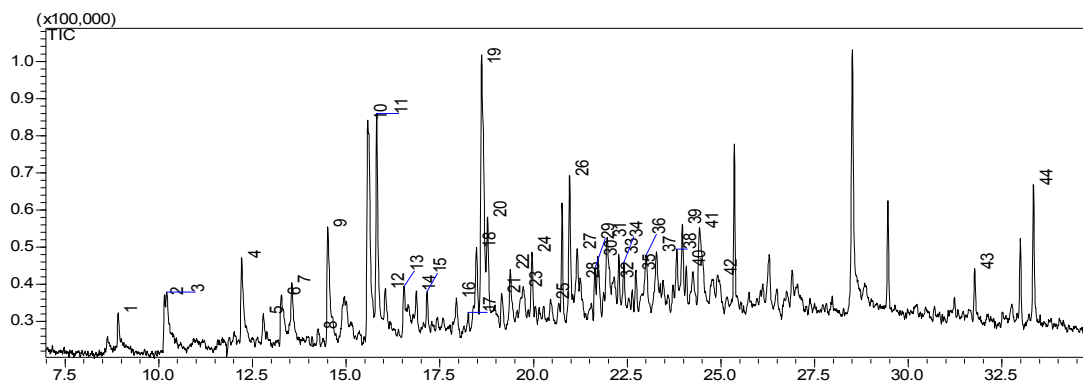
Rising the temperature, increases the synergetic effect over the oil production due to the extensive biomass fragmentation with the temperature increase. When temperature is sufficiently larger than the activation energy for the bond breaking, the biomass depolymerization occurs. At lower temperatures takes place the primary decomposition of the biomass and, when temperature is increased the fragments are broken into organic compounds of low molecular weight [12,14]. At higher temperatures it is expected that a high amount of gas can be generated. This is not observed probably due to the high amount of solvent used continuously to remove the cracked biomass inhibiting the repolymerization or secondary decomposition of bio-oil.

The increase in the bio-oil yield with rising temperature in the thermoconversion processes can be found in literature reporting that the optimum temperature range is closely related to the biomass type and to the

parameters used in each process. It is also reported that high temperature range decreases the oil yield favoring the increase in char due to repolymerization of the fragments of biomass [15-18]. But, the use of supercritical solvent or a mixture of solvents in the thermoliquefaction process can inhibit the formation of low-boiling point compounds, mainly gaseous, probably be due to the ability of supercritical fluids to dissolve biomass materials which would not be soluble in either liquid or gaseous phases of the solvents [19,20].

### 3.3 Bio-Oil Chemical Characterization

The GC-MS analysis allowed the identification of more than 80 different compounds, of different chemical classes including sugars, alcohols, ketones, ether, ester, phenols and hydrocarbons. The bio oil formed at 300 °C showed mainly sugars, the temperature of 400 °C provided the formation of alcohol as main compounds and phenolic compounds are mainly formed at 500 °C. A characteristic chromatogram of the bio-oil obtained at 500 °C with the main peaks identified is presented in Figure 3.



**Figure 3.** Chromatogram of the bio-oil produced at 500 °C, heating rate of 30 °C.min<sup>-1</sup> and cracking time of 30 min.

For the main peaks identified, the quantification was made in a semi-quantitative mode as concentration percent in area. The compounds are classified in chemical groups comprised of acids (peaks 1, 2, 8), esters (peaks 25, 32, 35, 43, 44), alcohols (6, 21, 23, 29, 30), ketones (9, 27) and phenols (all other peaks). Of all chemical groups, phenols correspond to about 60%. The high amount of phenols compared to other chemicals can be attributed to the more effective degradation of lignin present in the biomass that occurs at higher temperatures compared to cellulose and hemicellulose that are responsible for the formation of the other chemical species than phenols.

## 4. Conclusions

In this study, high yield of bio-oil was obtained by thermoliquefaction of palm fiber in supercritical ethanol at temperatures of 300, 400 and 500°C, heating rates of 10 and 30 °C.min<sup>-1</sup> and cracking time of 10 and 30 min. It was observed that increasing temperature, greatly increased bio-oil yield. Higher temperature also promoted the formation of more chemical species. The acid and water content in the bio-oil was considered low (about 2 and 1%, respectively). In this sense, the thermoliquefaction process of palm fiber in supercritical ethanol is very attractive but it is necessary to investigate the effect of other solvents beyond pressure and particle size.

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