Transformation of sugarcane bagasse into biocrude via organic solvents

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ABSTRACT

Nowadays there is a major focus in new biomass-derived fuels development and research, however, there are several obstacles that delay the introduction of this bio-oils into oil refineries. In the current work a recent concept of bio-oil, entitled biocrude, is divulged. This oil is produced by hydrolysis and ketalization of the sugarcane bagasse fiber, second-generation biofuel. With this method is obtained a bio-oil far more stable than the known pyrolysis bio-oil, and in addition, it has a greater miscibility in crude oil, therefore, its co-processing in an oil refinery is exceptionally compatible.

Essentially, this work is divided into two main parts. In the first part, the biocrude is produced in two regimens, in a batch reactor, and in a semi-continuous reactor. The key goal was to reproduce and optimize the tests carried out previously but currently executed on a larger scale. Thereafter, the physicochemical characterization of the oils was accomplished, in order to obtain fundamental information for the second part of the project.

In the second part of the study, a semi-continuous industrial process was designed, based on the semi-continuous laboratory process, with the aim of ascertaining the economic viability of this process which is still very preliminary. Having defined the location of the pilot plant in Brazil and the project capacity of 1.3 kton/year, it was possible to size all the main equipment.

Finally, the cost of producing the barrel of biocrude was obtained at a very competitive cost of US$ 50. Yet, is important to note, that this amount does not account any benefits that can come from a green project, benefits that can arise as well as tax benefits from the government, or as, tradable credits from the "new" carbon market.

Keywords: biocrude, sugarcane bagasse, second-generation biofuel, ketalization, hydrolysis.

1. Introduction

Currently, it is common knowledge that the increase in pollution, more specifically air pollution, is due to the use of energy from fossil sources, mainly from the burning of oil and coal. As a result of a global concern over the years, there has been a growing focus on renewable energy sources, such as hydro, wind, solar, geothermal, tidal and biomass energy.

The bio-oils produced from the different sources of biomasses have been studied in order to produce an oil that is the most analogous as possible to crude oil. Bio-oil produced from pyrolysis of biomass has been the most widely studied and developed, however, it represents some problems. The pyrolysis oil is a highly oxygenated bio-oil, which is subsequently very corrosive, poorly miscible with crude oil, thermally unstable and tends to polymerize when exposed to air. Its pretreatment is essential for the removal of the oxygen in excess, thus causing great difficulties and increased costs for its co-processing in refineries[1].

In the laboratory LaCES – Laboratório de Catálise e Energia Sustentável was studied and developed a bio-oil produced from the hydrolysis and ketalization of the sugarcane biomass [2][3][4].

In summary, through this process it is possible to achieve a bio-oil of similar appearance to the pyrolysis bio-oil, however, this one has several advantages that would differentiate from this and resemble the crude oil, being therefore called biocrude.

Although this study is a preliminary study, due to the results of several tests [2] [3], it is thought that, with the development of a production process of this oil and the determination of its production cost, it will be possible to introduce it into oil refineries.

In order to validate the insertion of this bio-oil into an oil refinery, catalytic cracking tests via an FCC (fluidized catalytic cracking) were performed with several mixtures of bio-oil and diesel. These studies have proven that the bio-oil can be converted to xylenes, benzenes, and other aromatic hydrocarbons, compounds already used in high-octane gasoline. In addition, the co-processing of diesel and bio-oil improved the performance and quality of gasoline

compared to pure diesel, and also reduced the number of oxygen compounds and coke compared to pure bio-oil, which demonstrates a synergistic effect [2].

2. Experimental Method

Biocrude is produced by a process composed of 3 phases:

- **Pre-treatment:** drying, grinding and granulometric classification of cellulosic wood biomass;
- **Reaction of hydrolysis and ketalization** of the hydrocarbons of the biomass fiber with a solvent in acid conditions;
- **Neutralization** of the medium and oil drying.

2.1. Physicochemical Characterization of Sugarcane Bagasse and Biocrude

2.1.1. Qualitative and Quantitative Analysis of Ketals in Biocrude by High-Performance Liquid Chromatography - Mass Spectrometry (HPLC-MS/MS)

HPLC-MS/MS analysis was performed on a high-performance chromatograph, model 1260, from Agilent Technologies, coupled to a QTRAP 5500 mass spectrometer, produced by AB Sciex, which is a spectrometer of quadrupole-trap hybrid masses (ion trap).

A column (100 mm x 2.1 mm, 3 μm particle size), model Hypersil GOLD, made by Thermo-Fischer was used, which was maintained at 35°C. The mobile phase used consisted of (A) aqueous solution of 5 mM ammonium formate and (B) acetonitrile. Chromatographic analysis was performed in gradient elution (0-0.5 min, 15% B; 0.5-10 min, 90% B; 10-11 min, 90% B; 11.1-15 min, 15% B) at a flow rate of 350μL/min. The injection volume was 8.0 μL.

Ionization was done by electrospray and operated in positive mode. The following parameters and their values are described: curtain gas (CUR) = 15 psi; collision activated dissociation (CAD) = mean; spray voltage (IS) = 5500 V; temperature of the source (TEM) = 400°C; gas source 1 (GS1) = 40 psi; gas source 2 (GS2) = 45 psi; decluster potential (DP) = 30 V; Input potential (EP) = 10 V; Collision cell output potential (CXP) = 10 V.

2.1.2. Thermogravimetric Analysis (TG) of Sugarcane Bagasse and Biocrude

Thermogravimetric analyses were performed on the Netzsch TG 209 F1 Iris equipment, with a temperature range between 35 and 800°C and at a heating rate of 10°C/min. The analysis was carried out under a nitrogen atmosphere, under a flow protection of the balance of 10 mL/min and purge flow of 60 mL/min. The samples used for thermogravimetric were ± 10 mg of macerated bagasse.

The mass losses associated with certain temperature ranges are considered as indicative of the amount of different chemical components present in the sugarcane bagasse and its degradation temperature.

2.1.3. Determination of Biocrude Viscosity

A rheometer of the TA Instruments brand, Discovery hybrid rheometer DHR-3 model was used to determine the viscosity of the oil. For the measurements, a Peltier steel plate with a diameter of 40 mm was used and the upper cone had an angle of 2.0°.

Five measures were taken in peak hold from 40 to 80°C, with a heating rate of 10°C.

2.1.4. Calorimetry

With the Pyris Diamond DSC calorimeter from Perkin Elmer, it was possible to obtain the specific heat capacity of both batch and semi-continuous biocrude. The calorimeter coupled with two equipment, a cooling accessory, the Intracooler 2P, and a thermal analysis controller, the TAC 7 / DX, also from the same brand.

After determining the temperature change of a substance of known heat capacity, a sapphire was then possible to measure the temperature change of the biocrude. Specific heat measurement was performed in a temperature range of 10 to 140°C with a heating rate of 10°C/min. This analysis was performed in a nitrogen atmosphere under a flow of 20 mL/min.

2.2. Determination of Density

The density was measured at room temperature $(25 \pm 2°C)$ and for this purpose, the sample was weighed in a graduated vessel, previously calibrated. After weighing, the density was determined using the ratio of a measured mass (on an analytical balance with four precision houses) and the filled volume of the vessel used (2 mL).

The procedure was performed twice, and then an average density value was obtained.

2.3. Sugarcane Bagasse Pre-treatment

Initially, the sugarcane bagasse that had been used in the tests needed to be pre-treated. The bagasse used was obtained at the Bonsucesso free market, a neighborhood in the city of Rio de Janeiro, in October 2015.

The pre-treatment of sugarcane bagasse consists of 5 steps procedures: 1st washing; drying; milling; screening; 2nd washing. Thereafter, each process methodology will be explained.

In the present work one of the goals was to verify the quality of the oil produced only from the sugarcane bagasse fiber, 2nd generation biofuel, thus it was

necessary to remove all the sugars that did not come from the fiber. It should be noted that this bagasse comes from the sugar industry, where the sugarcane is crushed with the purpose of removing the sugarcane juice, therefore this high sugar concentrate juice gets impregnated in the bagasse fiber.

In the first washing stage, the bagasse was washed twice in distilled water. This washing served only to remove solid particles and residues from the cane juice present in the fiber so that bacteria or another microorganism would not degrade the bagasse, then it could be stored for a longer period.

After this washing, the bagasse had to be dried. The material was left outside for 12 hours at ambient temperature and then was dried at 135°C for 30 minutes in an oven.

The dried material was milled in a knife mill (V611, Winner), and classified for granulometry in a vibrating sieve (J-1 B, from Thomas Scientific), where the fraction between the sieves with meshes of 0.125 mm and 0.850 mm was selected.

Finally, the second wash was carried out, the sieved bagasse was again washed to be able to remove the last traces of "free" saccharides from its surface. The determination of sucrose in the distilled water after each wash was performed on a liquid chromatography equipment (1200 Series, Agilent Technologies) coupled to a mass spectrometer (API 2000 ESI-MS/MS, Applied Biosystems/MDS Sciex) [3]. Ultimately the bagasse was dried at atmospheric temperature and stored.

2.4. Production of Biocrude in Laboratory Scale

In this work the scale of biocrude production was increased, this oil had previously been produced by the laboratory, LaCES-UFRJ, but on a smaller scale [3]. With these tests, it was possible to analyze whether this process was reproducible on a larger scale and whether similar or more satisfactory results could be replicated.

Therefore, tests were performed in two regimens, first in batch and then in semi-continuous regimen. When repeating this reaction for any of the reactors it was known, due to previous studies performed in the laboratory, that certain conditions would already be fixed and only some variables would be optimized. For example, in the case of discontinuous reactors less stringent temperature conditions had to be used, when compared to the semi-continuous reactor, to ensure that there would be no degradation of the product. Therefore, the temperature was one of the variables fixed for each system.

2.4.1. Reagents and Solvents
The following reagents and solvents were used in addition to the sugarcane bagasse: acetone (99%;

VETEC), sulfuric acid (95-99%, VETEC), ethyl acetate (99%, VETEC), sodium bicarbonate (99%, VETEC), sodium chloride (99%, VETEC) and anhydrous sodium sulfate (99%, VETEC).

2.4.2. Neutralization and Drying of Biocrude
It should be noted that, in the initial production tests of the discontinuous reactor oils, the neutralization method was different from the one of the succeeding oils. This was a result of smaller-scale tests that were being conducted in parallel, it was perceptible that there was a significant loss of oil with the first method.

A 100 mL aqueous solution of 5% w/w sodium bicarbonate (99%, VETEC) was added to the liquid portion and stirred to neutralize the oil till pH 7. After filtering all the oil from the precipitate into a decanting funnel, the aqueous phase was separated from the organic phase.

Sodium chloride (99%, VETEC) was added to saturate the aqueous phase. If more oil was retained at the aqueous phase, 50 ml of ethyl acetate was also added to increase the volume of the organic phase available to retain more oil. The precipitate fluid was filtered off and the same procedure was repeated three more times. Note that the organic phase to be withdrawn was added to the separated organic phase initially.

Anhydrous sodium sulfate (99%, VETEC) was added to the total organic phase, to remove all the water present. Subsequently, the organic phase was filtered into a flask, and ethyl acetate was used for the transfer.

Finally, the organic phase was distilled on a rotary evaporator, and pure neutral pH biocrude was separated from the solvents, acetone (99%, VETEC) and ethyl acetate (99.5%, VETEC).

When the methodology for the definitive neutralization was improved, only the way sodium bicarbonate was added changed. Instead of adding an aqueous alkaline solution the solid anhydrous salt was added, in this case, sodium bicarbonate (99%, VETEC). This eliminated the requirement to decant the aqueous phase of the organic phase, since the amount of water produced was insignificant and easily eliminated with a desiccant compound, in this case, sodium sulfate (99.5%, VETEC).

2.4.3. Discontinuous Reactor
In the discontinuous reactor, a 600 mL Parr reactor, model 4563 of Parr Instrument Co, 10 g of sugarcane bagasse was reacted with acetone (99%; VETEC) in the presence of sulfuric acid (95-98%; VETEC).

The conditions set for the Parr reactor were 120 psi (approximately 8.3 bar), mechanical stirring at 600 rpm (corresponding to maximum system

agitation) and temperature set at 90°C, with the reactor taking about 30 minutes until it reaches the temperature set in the controller. The reactor was pressurized at the start of the reaction by a gaseous mixture of 5% O_2/He on a molar basis.

Then the produced biocrude was neutralized and dried according to the first procedure already presented. The biocrude samples produced were analyzed on the HPLC-MS/MS (1260 Series, from Agilent Technologies, coupled to QTRAP 5500, from AB Sciex).

2.4.4. Semi-Continuous Reactor
At this point, it becomes clear the need to evolve into an increasing mechanization of the system, to reduce the time and cost of a future industrialized process.

The semi-continuous reactor used was a tubular reactor, at the inlet and outlet of this reactor there were two grids which retained the bagasse inside the reactor, resembling a fixed bed reactor. It should be noted that the flow of liquid reaction mixture, acetone (99%; VETEC) and sulfuric acid (95-98%; VETEC), which runs through the bagasse "bed", enters the base of the reactor and has an upward flow until the exit at the top.

The reactor has a volume of approximately 205 mL. The reaction, carried out previously in the batch reactor, was reproduced in this semi-continuous reactor. Since this reactor is a larger reactor, 20 g of sugarcane bagasse were reacted, instead of the 10 g used in the Parr reactor. A pump (LC-8A, Shimadzu) was used to pressurize the entire system (up to 8 bar), together with a backpressure valve. The heating system was based on a heating jacket and a heating resistance.

After the clarification of the semi-continuous equipment operation, the semi-continuous process will be described.

The pump was switched on and recirculated with acetone (99%, VETEC). The reaction temperature was expected to be constant (a deviation between 3 and 4°C was allowed).

The reactor inlet was then linked to an Erlenmeyer, in an ice bath, containing the reaction liquid mixture, acetone (99%; VETEC) and sulfuric acid (95-99%; VETEC). The outlet was placed in a new Erlenmeyer where the formed biocrude was collected and allowed to react for one hour at a predefined flow rate. It should be noted that the ratio of sulfuric acid/acetone (v/v) is higher in this semi-continuous than in the batch process, this alteration had previously been studied [3].

After 1 h the inlet piping was changed to an Erlenmeyer flask containing pure acetone (99%; VETEC) and recycled acetone from the system. The flow rate was increased to shorten the amount of time that would take to remove the still formed oil trapped in the system.

The bio-petroleum produced was neutralized and dried according to the second procedure presented previously.

At the end of each reaction, the mass of dry bagasse that was not consumed and the mass of biocrude produced was weighed. Later the biocrude samples produced were analyzed on the HPLC-MS/MS equipment (1260 Series from Agilent Technologies, coupled to AB Sciex QTRAP 5500).

3. Results and Discussion

There are two main objectives in this study, firstly, to carry out the reproduction of biocrude, on a larger scale, and subsequently, verify the conditions already used on a small scale. After that, with the obtained biocrude, perform the maximum physical-chemical tests possible, for a better characterization and understanding of the same.

3.1. Experimental Results and Discussion
First, it is important to explain how the productivity of each reaction was evaluated. Efficiency was measured by three parameters: the amount of biocrude produced in relation to the bagasse used, the reaction yield; the amount of bagasse reacted as a function of the initial bagasse, the conversion of the reaction; and the number of ketals formed.

The percentage of ketals was calculated by analysis on liquid chromatography equipment (1200 Series, Agilent Technologies) coupled to a mass spectrometer (API 2000 ESI-MS/MS, Applied Biosystems/MDS Sciex) and allowed to know whether acetone had been incorporated in the oil and formed these protecting groups, ketals, and the type of ketal formed [2], [3].

Ketals detected by HPLC-MS/MS are divided into 4 different molecules, xylose (XDK) and glucose (GDK) di-ketals, the trade name of 1,2:3,5-di-O-isopropylidene-α-D-xylofuranose and 1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose, respectively. And the mono-ketals of xylose (XMK) and the mono-ketals of glucose (GMK), the trade name of 1,2-O-isopropylidene-α-D-xylofuranose and 1,2-O-isopropylidene-α-D-glucofuranose, respectively.

Analyzing all these data, it should be noted that the severity of the conditions applied was also considered, each condition variation would need to be balanced out by the gains obtained in each test. When speaking of severity, this does not only mean high temperature or pressure conditions, or even a strong acid concentration but for example, it could be an excessive increase in the reaction time that only resulted in a slight gain.

3.1.1. Sugarcane Bagasse and Biocrude – Properties

Before exposing the results obtained in each reaction it will be presented, in the two tables below, some properties of the bagasse and the product.

Table 1 – Physicochemical properties of bagasse.

	Bagasse
Physical state at 25°C	Solid
Bulk density at 25°C (kg/m³)	130
Specific heat at 20°C (KJ/(kg.K))	0.46 (dry)

Table 2 - Physicochemical properties of biocrude, determined by the tests described in the experimental method.

		Biocrude	
Physical state at 25°C		Liquid	
Density at 25°C (kg/m³)		1100-1200	
		Discontinuous Reactor	Semi--continuous Reactor
Specific heat at 25°C (J/(g.K))		1.351	1.814
Viscosity (Pa.s)	40°C	0.97	-
	80°C	0.06	-

Although the density at 60°F (15.55°C) was not determined from the following equation, the API grade of this oil was calculated using the lowest density value (1100 kg/m³) determined at approximately 25°C.

$$°API = \frac{141.5}{\rho_{sample}} - 131.5 \qquad (1)$$

It should be noted that the relative density of the sample, in this case, biocrude, is the density measured comparatively to the density of the water, so the ρ_{sample} is 1100 kg /m³/1000 kg/m³, thus obtaining a negative API degree.

In general, the classification of the API grade contributes to the product price categorization in the market. The higher the API grade, the higher the value of the product on the market, however oil with a °API between 40 and 45° leads the higher prices. Above 45°, molecular chains become shorter and less valuable for refineries.

Oils that have a °API of less than 10° are very heavy oils, they consist almost entirely of aromatic hydrocarbons, so it could not be introduced into a refinery as 100%, as would be expected. Considering this scale, and regarding the future valorization of biocrude, it could be diluted in a lighter hydrocarbon to produce an oil with a higher grade API.

Looking at this from a different perspective, it is clear that such comparisons and assumptions are very useful when it comes to different types of oil, but biocrude is a biofuel and not a crude oil. When referred to a heavier oil, it refers to a very viscous oil (higher processing costs), which contains more heavy metals, sulfur, nitrogen, and high acidity, and these are the characteristics that lead to a low degree API being associated with a low market value oil. However, biocrude does not contain these components (it may contain but in negligible proportions), as it is produced from lignocellulosic materials. Therefore, in the case of biocrude, the chemical functions and the composition are different and this cannot be evaluated by this scale. Another scale would have to be defined in the case of this biofuel in order to have a reliable assessment of it.

In addition, the viscosity of the biocrude, despite being high at room temperature, with a slight increase in processing temperature, is drastically reduced, thus causing minimum problems in the pumping and handling of biocrude. At 40°C a viscosity of 0.97 Pa.s is obtained, as shown in Table 2, while at 80°C it already has a viscosity of 0.06 Pa.s. It should be noted that, although the viscosity of the biocrude is on average higher than the viscosity of the pyrolysis bio-oil (0.035 to 1 Pa.s at 40°C, depending on the raw material), this is justified by a high water content present in the pyrolysis oil, from 15 to 30% [5] (note that on average crude oil contains not more than 0.5% of water in its composition [6]). Of course, this water content will provide a lower viscosity than the biocrude, thus improving its transport properties, however, it will greatly decrease its energy value.

Although it has been concluded that the use of the API grade would not be very useful in the classification of biocrude, it is advantageous to compare the grade API with the specific heat of a heavy oil and biocrude, since is currently the only comparative term available.

The API grade is directly linked to the calculation estimate of the oil specific heat. The lighter the oil, the greater its specific heat.

For the biocrude, it was used the determination of this value from a calorimeter, obtaining the values of specific heat at 15.56°C of 1.469 and 1.712 J/(g.K) in a discontinuous regime and semi-continuous regime, respectively, values not distinctive from those of light and heavy oils.

Now proceeding to the analysis of the calorific power of the pyrolysis bio-oil, resorting to tests

referenced in the literature [6], it was observed that, on average, this value is less than half of the calorific value of crude oil, and as already was mentioned, this is a consequence of the high water content in the bio-oil composition.

Also, remember the importance of the relationship between specific heat (or calorific value) on a volumetric basis and the density of a material. The fact that biocrude (and bio-oil pyrolysis) is a very dense fuel, promotes the reduction of transport costs, saving the volume needed to transport an oil with a high volumetric energetic potential.

3.1.2. Discontinuous Reactor

The initial tests were performed in a discontinuous reactor under the most favorable conditions that had already been studied[2]. In addition to the described conditions, 8.3 bar, 90°C, and mechanical stirring at 600 rpm, 200 mL of acetone (99%; VETEC); and 0.8 ml of sulfuric acid (95-99%; VETEC) which were reacted for 2 hours and 30 minutes with the 10 g of bagasse. Subsequent to this test, there were made 3 more tests in the batch reactor all based on this standard test.

In the second test, the reaction time was increased by 90 minutes, the reaction was given a duration of 4 hours.

In the third test the ratio of biomass/acetone (w/v) was increased, a volume of acetone (99%; VETEC) of 150 ml was used and consequently a lower volume of sulfuric acid (95-99%; VETEC), 0.6 mL, to maintain the sulfuric acid/acetone ratio of 0.4% (v/v).

In the second test the yield was increased, see

Table 3. It was decided to further increase the reaction time, in this last test the reaction duration was increased to 5 hours.

In these 4 tests, after obtaining the oil, the first procedure of neutralization and drying of the bio-petroleum was used.

The results obtained in these first 4 tests, the mass of oil formed, bagasse mass after the reaction, yield (η), bagasse mass consumed in the reaction and conversion of the reaction are shown in

Table 3.

Analyzing the results, it is observed that biocrude 2 is the one with the highest yield, very similar to 4 and 1. In terms of conversion, biocrude 4 is the leading, and 2 and 3 also have similar values.

After completion of these 4 tests, the percentage of ketals formed in each reaction was quantified, these values are found in Table 4.

Table 3 - Experimental results of the first four reactions in a discontinuous reactor.

	1	2	3	4
m_{oil} (g)	3.99	4.12	3.08	4.11
$m_{residual\ bagasse}$ (g)	6.85	6.30	6.46	6.20
η (%)	39.89	41.23	30.83	41.13
$m_{consumed\ bagasse}$ (g)	3.15	3.70	3.54	3.80
Conversion (%)	31.50	37.03	35.43	37.95

Table 4 - Results of the quantification of xylose (XDK) and glucose (GDK) di-ketals, and xylose (XMK) and ycosecoseglucose (GMK) mono-ketals by HPLC-MS/MS from the first four reactions in a batch reactor.

Ketals (%)	1	2	3	4
XMK	6.0	6.8	5.3	5.5
GMK	0.2	0.2	0.1	0.1
XDK	20.7	14.7	14.4	11.7
GDK	14.5	10.4	9.7	7.6
Total	41.4	32.1	29.4	25.0

3.1.3. Semi-continuous Reactor

In the semi-continuous reactor, the tests were started with the most favorable conditions, that had already been studied [2] and with direct adaptations to the size of the reactor.

In addition to the conditions already described, 8 bar and 20 g of sugarcane bagasse, several conditions were used. The conditions were being defined as the results were obtained on a smaller scale process. The smaller quantity tests were being carried out in parallel with these tests of a higher scale.

Four tests were carried out in the reactor, but only the most reliable results are presented. In this test, the conditions used were 120°C, the ratio of sulfuric acid and acetone was 1/500 %v/v. A flow rate of 7 ml/min per 1 hour was chosen due to test results obtained from other work not yet publicly disclosed. Table 5 below shows the reaction results:

Table 5 - Experimental results of the reaction in the semi-continuous regime.

	Semi-continuous Test
m_{oil} (g)	9.2
$m_{residual\ bagasse}$ (g)	11.0
η (%)	45.9
$m_{consumed\ bagasse}$ (g)	9.0
Conversion (%)	45.2

Given that the biocrude was neutralized and dried according to the second methodology. As was said, the amount of sodium bicarbonate used, 100.1 g, was much higher than the value calculated by

stoichiometric calculations, according to calculations it should have been approximately 3.2 g. Therefore, it is possible to conclude that the agitation was very weak, being necessary to use an excess of 317%, a very maladjusted value of what would be necessary for this procedure.

The HPLC-MS/MS analyses of the semi-continuous biocrude were then executed, see Table 6.

Table 6 - Results of the quantification of xylose (XDK) and glucose (GDK) di-ketals xylose (XMK) and glucose (GMK) mono-ketals by HPLC-MS/MS of the reaction in the semi-continuous regime.

Ketals (%)	Semi-continuous Test
XMK	8.7
GMK	0.7
XDK	27.7
GDK	14.3
Total	51.4

As expected, a higher percentage of ketals can be obtained resulting in an improved quality of the oil. The equilibrium of the ketalization reaction is favored in basic conditions, probably the shortest time in contact with acid, in the semi-continuous reactor, increased the yield in ketals and the conversion of the biomass.

When calculating the incorporated acetone in the reaction (this percentage was equal to the efficiency of the oil mass formed versus bagasse mass consumed), it was concluded that this value is very different from the ketals quantification result. This result, clearly, was a consequence of operator errors, probably due to oil losses resulting from a poorly efficient post-reaction recovery. As it happened to have a much higher amount of bagasse, it became more difficult to clean all the oil from the bagasse fiber.

One can also make a very simplistic estimation of this percentage, taking into account the quantification of ketals. Knowing that one mole of acetone is required to form one mole of mono-ketal. It can be deduced that x% acetone formed 9.4% mono ketals and 2x% acetone formed 42% di-ketals, this provision resulting in a 30.4% incorporation. Although simplistic, this calculation resulted in a value equivalent to the already proven value by previous tests [2], this value is also around 30% of acetone incorporated.

4. Process and Cost of Production of Biocrude

Finally, it became important to outline a process of biocrude production in a semi-continuous regimen on an industrial scale. This was done by implementing some conditions from the laboratory scale semi-continuous reactor, in order to determine the cost of production of this biocrude. However, since this is an industrial scale process, some topics were readjusted.

4.1. Process of Production of Biocrude in Pilot Scale

A flowsheet of the biocrude production process is presented in Appendix A and then the whole process is described and substantiated. The biocrude production process is divided into 5 zones: reagent storage zone (zone 100), pretreatment zone (zone 200), reaction zone (zone 300), separation zone (zone 400), and product storage zone (Zone 500).

4.1.1. Capacity and Assumptions of the Mass Balance of the Biocrude Production Process

Usually, when determining various data for the evaluation of the production process, such as the market price of the product and manufacturing capacity, a market analysis of the price is made. This analysis will ascertain at which price the product is currently sold, and will reveal the existing manufacturing capacities, but since this is a new product such data is not available. For this reason, it was decided to take as a starting point for the economic evaluation, of this plant, a daily production capacity of 3 tons of biocrude. A reasonable size for a pilot plant and a quantity that is plausible from the point of view of profitability.

From this information, it is possible to reiterate the capacity of the process, for which two data are needed: the annual production and the occupation rate. If in one day is produced 3 tons/day, in one year of production 1 kilotons would be produced. This value was obtained considering that the factory is producing 24 hours a day, 335 days a year since it is necessary to subtract the days in which the shutdown and startup are made (1 month). As the average occupancy rate, for the initial years, is 80%, the factory project capacity will be around 1.3 kton/year.

Now it is possible to summarize all the assumptions of this process, some of them already mentioned in the previous subchapter:

Reagent Storage (zone 100):
- The reagents were assumed to be 100% pure.

Pretreatment (zone 200):
- The initial bagasse contained 40% moisture;
- Dry bagasse had 7.4% moisture (determined by the thermogravimetry, the mass loss till 105°C);
- In the dryer, the air temperature at the entrance is 145°C and at the exit is 120°C;
- The atmospheric heated air contained 3% water at the entrance to the dryer;

- In the burner, the oxidizer used was atmospheric air and the fuel was methane.

Main Reactors (zone 300):
- The reactors operate at 120°C and 8 bar;
- The mass/volume ratio of bagasse/acetone is 1:25;
- The volumetric ratio of acetone/sulfuric acid feed is 500:1;
- Bagasse conversion is 45%;
- The yield of biocrude produced is 46%;
- Acetone incorporated into biocrude is equivalent to 20% (w/w) of the biocrude produced (this percentage was equal to the efficiency of the oil formed versus bagasse consumed) [2];
- The water consumed in the hydrolysis is considered equivalent to that formed in the ketalization, so it is assumed that the amount of water contained in the bagasse is the same amount of free water that leaves the reactor effluent;
- The water solubility in acetone was considered negligible;
- The bagasse after reaction draws 0.1% acetone and 0.05% water.

Neutralization Reactor (zone 300):
- The reactor operates at atmospheric pressure and at room temperature;
- The amount of water formed in the neutralization is stoichiometric;
- Calcium oxide is added with 10% excess.

Non-Consumed Bagasse Filtration (zone 400):
- The rotating filter operates at 0.8 bar;
- It is possible to separate 100% of the bagasse from the water and acetone;
- There is no loss of water or acetone by evaporation.

Separation of Solids from Neutralization (zone 400):
- In the thickener it was assumed that 72% of the suspension is clarified and that this phase does not contain any solids;
- The rotating filter operates at 0.7 bar;
- In the filter, 100% of the solids (calcium oxide and calcium sulfate) can be separated from water, acetone, and biocrude;
- There is no loss of water or acetone by evaporation.

Separator Gas-liquid (zone 400):
- The separator has a heat exchanger that precedes it, and which heats the entire mixture to 75°C;
- 100% of the biocrude is separated in the base of the column and 100% of the acetone and water leaves at the top.

Vacuum distillation column (zone 400):
- The liquid ring pump system produces a vacuum of 0.6 bar;
- In the distillation, an acetone with 100% purity is obtained at the top of the column, which is then recycled to the main reactors.

4.1.2. Location and Climate

This project was designed for the implementation of a pilot unit in Brazil. It is in Brazil where the cheapest raw material is found, being the largest producer of sugar in the world.

4.1.3. Construction Materials

Since very high operating temperatures or pressures are not used, the equipment building materials choice is not necessarily dependent on these values.

Sulfuric acid and calcium hydroxide are present, so, as a conservative measure, the 316 stainless steel was chosen as the equipment material in which these were present. In the others, carbon steel was chosen.

4.1.4. Economic analysis

In order to determine the investment required for the process and the production cost of this biocrude, the data obtained in the semi-continuous test, on a laboratory scale, were used. However, some adaptations to this industrial scale were made.

4.1.5. Investment Estimate

The total investment is composed of the fixed capital, the working capital, plus the interim interest.

4.1.6. Fixed Capital

The fixed capital is the sum of tangible and intangible capital, there are various ways to estimate this cost, but, in general, any method is based on the estimated base equipment cost.

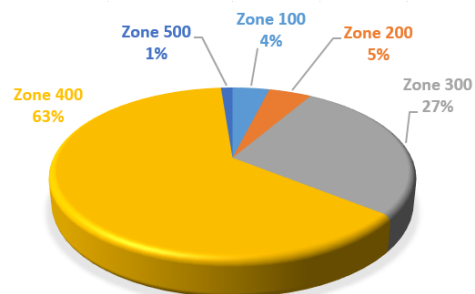i. **Estimated Base Equipment Cost.**

Figure 1 – Equipment cost by zone (2.1 M€).

From Figure 1, it can be seen, that zones 300 and 400 correspond to the most expensive areas of the process. This fact is expected since the reaction zone starts from a semi-continuous and not from a continuous process, forcing the existence of two identical reactors. In the

zone 400, it is necessary numerous equipment to make the separation of the oil of the remaining equipment, giving rise to this higher cost of the process. These are the two areas where the future optimization of the equipment will be more important.

    ii.   **Detailed Estimate of the Fixed Capital.** In this method for the determination of the various installments that make up fixed capital, percentage ranges are allowed on the cost of the basic equipment (C_b) or on total fixed capital (I_f).

After estimating these fractions, the Total Fixed Investment was obtained, resulting in 8.6 M€. Where 6.5 M€ are Tangible Fixed Investment and 2.1 M€ are Intangible Fixed Investment.

4.1.7. Working Capital

Was determined taking in account the process raw material consumption, stock of products manufactured, quantitative of products in labor, credit offered to costumers and obtained from suppliers, and the working capital. The total working capital was 0.1 M€.

4.1.8. Interim Interest

This portion of the total investment was calculated based on the investment plan, considering that equity represents 50% of the total investment. The remaining capital is financed by external capital with an interest rate applied for the financing of 1,05%, corresponding to the basic interest rate in Brazil, SELIC (Special Settlement and Custody System), plus the average spread, 31.9%.

This resulted in a total interim interest of 1.5 M€, and a total investment of 10.2 M€.

4.2. Estimated Cost of Production

It consists of the parts of manufacturing cost, which relate to all the charges directly required by the production activity, and the portion of the overhead costs which represents all the costs required to support the production activity.

4.2.1. Manufacturing Cost

Manufacturing costs include the direct costs, indirect costs, and fixed costs.

The direct costs are composed of raw materials, manufacturing workforce, control workforce, utilities and services, maintenance, solvents, and miscellaneous supplies.

The following graph shows the weight that each portion of direct costs represents:
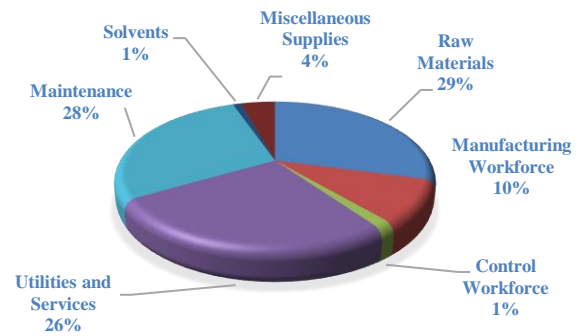

Figure 2- Percentage distribution of the various components of direct costs.

It was concluded that the raw material share is the one that has the greatest weight in the direct costs. The total of direct cost was 2.2 M€ in 2018.

- **Indirect Cost:** The indirect costs represent the costs of labor sustenance of the production activity. It corresponds to about 50 to 70% of the sum of total labor and maintenance costs. In this present study, an average percentage of 60% was admitted. This resulted in an indirect cost of 0.4 M€ in 2018.
- **Fixed Costs**: Comprises the expenditure which is independent of productive activities. The following are the elements that constitute this topic: depreciation; insurance and taxes, and rents. This resulted in a fixed cost of 0.8 M€ in 2018.

4.2.2. General Costs

Overheads include the following installments: administrative expenses (40% of the manufacturing workforce); commercial costs (will start at 15% till 7% of the total cost of production, decreases with the time); expenditure on R&D (it was considered a profit margin between 30 to 40%, since it's a small factory, and since this is a new product the highest percentage of R&D was chosen, 5% of the total cost of production) and financial charges (calculated assuming annual repayments to the bank over the course of the project and an interest rate of 1.05%, and it was admitted a year as grace period).

The items included in overheads were calculated based on percentages of other costs, this resulted in a general cost of 1.8 M€ in 2018.

For the interim year under study, direct costs represent the largest portion of production costs, this is mainly due to the cost of raw materials. The next table presents the total of the manufacturing cost, and the

latter with the general cost, i.e., the production cost for 10 years:

Table 7 – Estimative of Production Cost[7].

M€/year	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027
Manufacturing Cost	5,3	5,4	5,1	4,8	4,9	4,9	5,1	5,3	5,4	5,6
Production Cost	3,5	3,7	3,1	3,4	3,7	3,9	4,1	4,3	4,5	4,7

Finally, the results of the cost of the biocrude barrel where obtained, in the year of 2018 the barrel of biocrude would cost US$ 50 and in 2027 would be US$ 53. Being that on July 9, 2018, the price of a barrel of oil was US$ 73.72[8].

By analyzing the graph (Figure 3), it can be concluded that the price of the solvent greatly influences the cost of production of a barrel of biocrude. Therefore, in addition to improvements in procedural terms, it will also be very important to use an alternative solvent to acetone.
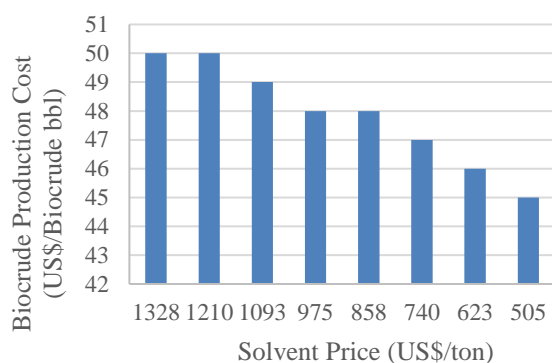

Figure 3- Solvent price versus Biocrude production cost.

5. Conclusion

As can be seen from the results of the discontinuous and semi-continuous reactor, the conversion and yield (from about 32 and 40% in the batch to 45 and 46% in the semi continuous, respectively) are higher in the semi-continuous. This is probably due to the increase of temperature in the reaction of the semi-continuous, this increase is allowed owing to the reduction of the residence time in the reactor. This reduction of time also reduced the degradation of the oil produced, and increased the opening of the sugarcane fiber, thus obtaining a greater breakage of the crystalline polymers of the cellulose, more difficult to reach.

Concerning the formation of hydrocarbon ketals, we can also conclude that there was an increase in their production in the semi-continuous reactor (from 41.4% in the discontinuous to 51.4%), with a quantitative

increase in the incorporation of acetone in the oil. This increase can be justified by the higher yield in the semi-continuous, and consequently resulted in a greater number of xylose and glucose molecules available to be hydrolyzed.

As this semi-continuous process is analyzed, it is concluded that at the present it is only an initial concept and not the definitive process.

It is hoped that, in the near future the installation of a pilot plant, of this process, would be feasible and thus the desired improvements would be achieved, both technological and energetic. Optimizing the process with more functional equipment and an integration of utilities where there is maximum reuse of all streams and effluents. It is also worth noticing that, both bio-oil and bagasse that are not consumed can be used as energy sources for a more sustainable plant.

After obtaining the process flow diagram (Appendix A), it was possible to carry out the economic evaluation, where the investment (and base equipment cost) and the respective investment plan were calculated, it was determined that the investment needed for the proposed installation is about € 10.2 million, of which 50% comes from outside capital.

Finally, the cost of production was obtained, and even without an optimization of the process, and even with the oil crisis that we are still experiencing, the cost of producing a barrel of biocrude is US$ 50.

This is a cost that can rival the current cost of oil, US$ 73.72 (July 9, 2018)[8], although it is thought that this drop in oil prices will be temporary, resembling all crises throughout the oil exploration, this is still a big price gain. Remembering that, these price fluctuations are mostly derived from exploratory country policies and global government strategies.

Finally, it should be noted that no in-depth investigation of the incentives inherent to a plant using green technology had been executed. Even so, it has been possible to see that there are some governmental, fiscal and other funding to boost investments in projects that are "environmentally friendly"; and that, in addition to this added value, there is also the carbon market, where green companies negotiate their green credits for significant monetary amounts.

Acknowledgements

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1. Appendix A - Process Flow Diagram – Biocrude Production