

Coal and Acai Seed Cofiring into Bubbling Fluidized Bed Boiler

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Abstract

In line with the Greenhouse Gas Protocol (scopes 1 and 2 emissions), Hydro aims to reduce its CO₂ emissions by 30 % in 2030. Alunorte, Hydro's alumina refinery in Para, Brazil, will make a significant contribution to this goal, reducing its direct and indirect CO₂ emissions by 70 %. Alunorte burns approximately 720 kt/year of mineral coal in three fluidized bed boilers to produce high-pressure steam for energy generation and subsequent use in its thermal processes. The objective of this work was to show a way of decarbonization by replacing coal with local biomass, acai seed (*Euterpe oleracea*). Acai seed is a locally abundant agroforestry residue, with an availability of 1.4 Mtpy. Using such residue as boiler fuel fits the circular economy concept and will benefit the local community in the environmental, economic, and social spheres. The methodology consisted of acai seed energy characterization in the laboratory, computer simulation of the combustion, and industrial test execution with biomass and coal cofiring, in which the biomass contributed up to 20 % of the boilers' overall energy input. The results contain boiler operational parameters, ash properties, and atmospheric emissions. Besides the avoided emission of 52 000 t CO₂ up to this phase of tests, this work shows the feasibility of using acai seed as fuel regularly and safely for bubbling fluidized bed boiler operation. These activities are part of the ongoing development stage to gather technical knowledge to support the conversion studies of the coal-fired boilers for exclusively biomass feeding and prepare the supply chain for this new raw material with the future quantity and quality needed for 2030.

Keywords: Biomass, Circular economy, Combustion, Decarbonization, Sustainability.

1. Introduction

Hydro aims to reduce its direct and indirect greenhouse gas emissions by 10 % in 2025, 30 % by 2030, and become carbon neutral by 2050 or earlier. Alunorte, Hydro's alumina refinery in Brazil, with a nominal capacity of 6.3 Mtpy, will significantly contribute to the company's global target by improving its energy and steam matrix. By 2025, Alunorte will have switched the fuel oil used in six boilers and seven calciners to natural gas, a fuel typically used in the global energy transition. Furthermore, three new electric boilers with immersed electrode technology will start operating and will be powered by renewable solar and wind energy. Both initiatives will reduce 1,4 Mtpy CO₂ emissions, representing a more than 30 % drop in refinery emissions compared to the 2017 baseline and reaching 0.45 t CO₂/t alumina.

For 2030, Alunorte's CO₂ reduction ambition is even more robust, foreseeing decarbonizing 70 % of scopes 1 and 2 emissions from 2017. In addition to the extension of the electrification plan for part of its matrix, Alunorte is also studying biomass as a potential alternative to replace bituminous mineral coal, whose annual consumption was 720 000 t in 2017. This fossil fuel currently feeds three high-pressure boilers (8.79 MPa and 485 °C) to generate energy and steam for the Bayer process, two of which are Bubbling Fluidized Bed (BFB) with a nameplate of 240 t/h each, and the other a Circulating Fluidized Bed (CFB) with a steam production capacity of 340 t/h.

Acai residue (seed) was the first biomass chosen to begin the studies due to the presence of the fruit in great abundance and the growing industry in Para, where the refinery is located, whose annual production is around 1 400 000 t/year [1]. CO₂ emissions from biomass combustion are considered neutral due to the recapture of this gas through photosynthesis during fruit planting, configuring a short carbon cycle. Among the biomasses from agroforestry residues available in the region, acai seed proved to be a good option also due to its shape (spheric) and thermochemical properties. In addition to decarbonizing the refinery and slowing down the effects of global warming, transforming the acai seed into energy will generate income and environmental benefits for the community (circular economy) by developing and strengthening this still-incipient type of business in the region. The accumulation of acai residue represents an environmental impact once it is often disposed of in open space, producing contaminating liquid and gas such as methane during its degradation and eventually causing spontaneous fire.

Approximately 85 % of the acai (/ˌæs.aɪˈiː/, *Euterpe oleracea*) is made up of seed, and it is a fruit typically found in the Amazon region (more than 90 % of the world's production of this fruit comes from Para) [1]. The literature still lacks technical data and experience in terms of its energy characterization, transformation into biomass and combustion in sizeable high-pressure boilers. This fact, combined with Alunorte's objective of converting current coal-fired boilers to renewable fuel instead of acquiring new equipment, brings technical complexity to the project. Therefore, in partnership with the Federal University of Para (UFPA), a mid-term work plan was elaborated for the cofiring of acai seed and mineral coal in the existing BFB boilers aiming to mature and enable the use of this biomass with the quantity and quality necessary for the definite conversion of one or more coal boilers by 2030.

Firstly, both fuels were characterized in the laboratory, as well as the combustion of pure biomass and mixed with mineral coal in different blend percentages. The implications of inserting biomass into boilers were evaluated based on computer simulations, equipment design information, and operational history, with the aim of identifying whether there were limiting factors for the mixture fraction. Finally, industrial cofiring tests with a gradual increase in the contribution of biomass to the blend were carried out in bubbling fluidized bed boilers, maintaining constant monitoring.

2. Equipment

The two boilers used in this work are bubbling fluidized bed boilers manufactured by Alstom in 2006 [2]. The dense bed cross-section is 21.65 × 8.09 m with a height of one meter. Above the freeboard are two risers. Afterward, the flow passes through a battery of cyclones that removes and returns suspended solids to the dense bed and directs the gases to the cleaning system and chimney, as shown in Figure 1.

In regular operation, the boilers are fed exclusively with bituminous mineral coal, which enters the combustion chamber above the dense bed. Along with coal, limestone is injected into the combustion chamber to sequester sulfur and nitrogen. Primary air is injected through the base of the dense bed, which is responsible for fluidizing the bed and starting volatiles combustion. Secondary air is introduced into the furnace at a height of 1.8 m. The maximum furnace temperature expected in these boilers is 950 °C.

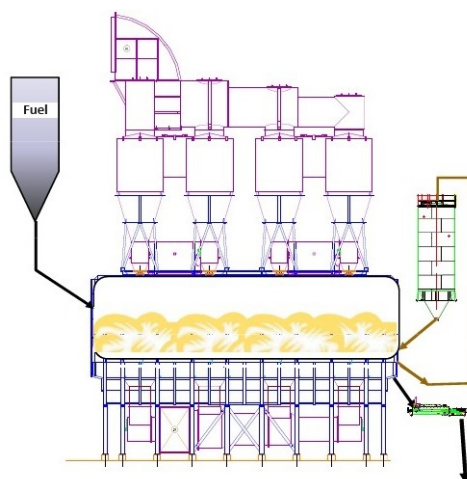


Figure 1. Scheme of the bubbling fluidized bed boiler [3].

3. Fuel Analysis

Currently, the mineral coal from the Drummond mine in Colombia is used in the BFB boilers in Alunorte, and a sample was obtained in the refinery's storage area for laboratory characterization along with acai residue biomass.

After the acai pulp processing in food industries and before getting to Alunorte, specific industries transform the acai seeds into biomass with a suitable energy content through a drying process. In this process, its moisture content is reduced from above 45 % to about 23 %, and depending on the beneficiation route, it can be commercialized with or without fiber. Samples of both types of seeds were collected from an industry near Alunorte for fuel analysis at UFPA.

Therefore, there are three fuels considered in this work: Drummond coal and acai seed (AS) with fiber and without fiber (see Figure 2).



Figure 2. Samples of Drummond coal and açaí seed with and without fiber.

Proximate, ultimate, heating value, density, and particle size analyses were carried out [4, 5]. Due to the different combustion characteristics between coal and acai seed, a thermogravimetric analysis was also carried out, which aimed to understand the behavior of each fuel individually during the combustion process [6, 7].

3.1 Thermochemical Properties Analysis

The procedure for the proximate analysis of coal followed standards NBR 16508, 16587, and 16586, and for biomass followed standards CEN\TS 14774-1, 15148, and 14775. Initially, the samples were separated and went through the process of moisture analysis, while the remainder

was placed in the oven for the moisture removal process. The data obtained include moisture, volatile, fixed carbon, and ash contents on a mass basis [2, 5, 8].

The ultimate analysis was performed on a PERKIN-ELMER Series 2400.1 ultimate analyzer. This made it possible to generate quantitative data in mass percentage of carbon, hydrogen, nitrogen, sulfur, and oxygen (by difference).

The Higher Heating Value (HHV) analysis was carried out using a calorimetric bomb model C2000, brand Ika Werke. All analyses were performed in triplicate to ensure the consistency and reliability of the results. The reproducibility of the experiments demonstrated the robustness of the obtained data. To obtain the Lower Heating Value (LHV), Equation (1) was used [7].

$$LHV = (1 - w_{bu}) * HHV - [9 * h * (1 - w_{bu}) * h_{lv}] - w_{bu} * h_{lv} \quad (1)$$

where:

- LHV Lower heating value, kJ/kg
- HHV Higher heating value, kJ/kg
- w_{bu} Moisture content, %
- h Hydrogen content, %
- h_{lv} Enthalpy of water vaporization, 2 453 kJ/kg

Table 1. Fuel analysis.

Class	Property	Drum. Coal	AS with fiber	AS without fiber
Proximate Analysis	Moisture (%) wet basis	13.53	23.0	23.0
	Volatiles (%) dry basis	36.49	77.52	78.20
	Fixed carbon (%) dry basis	50.26	21.68	20.33
	Ashes (%) dry basis	12.2	0.8	1.47
Ultimate Analysis	Carbon (%) dry basis	63.87	48.95	46.38
	Hydrogen (%) dry basis	5.29	6.90	7.17
	Oxygen (%) dry basis	15.96	42.07	43.76
	Nitrogen (%) dry basis	1.38	1.80	1.01
	Sulfur (%) dry basis	1.25	0.21	0.22
Heating Value	HHV (MJ/kg _{fuel})	26.40	19.54	19.33
	LHV (MJ/kg _{fuel})	21.50	13.31	13.10

The proximate analysis in Table 1 shows a high volatile content of acai seed in relation to coal. It causes an initial faster combustion for the acai and, therefore, greater reactivity [9]. It was also observed that acai has a smaller amount of ash than Drummond coal, which reduces the volume of inert material in the bed. This fact is expected to be irrelevant for the conversion and during the cofiring operation between biomass and coal in the bubbling fluidized bed boiler. However, it will represent a challenge for the conversion of the circulating fluidized bed boiler to operate exclusively with acai seeds. Ultimate analysis shows seeds with more oxygen and less carbon than coal. It causes a greater requirement of seed mass to meet the same energy as coal and less air, therefore, less nitrogen. The heating value analysis demonstrated that the greater moisture content in the acai seed results in a reduction in the LHV, which implies a trend to reduce boiler efficiency.

As the sulfur content is lower in biomass than in coal, neither an increase in SO_x emissions nor an increase in limestone dosage is expected with the blend between the two fuels.

3.2 Thermogravimetry

A thermogravimetric analysis was carried out on a vacuum-sealed thermo-microbalance, Libra-Neitzsch, TG 209 F1. Graphs of mass loss in percentage (TG) and mass loss rate in percentage per minute (DTG) were then obtained, varying with the temperature. The parameters used in the analysis were: temperature range of 25–800 °C, heating rate of 10 °C/min, oxidative atmosphere with volumetric flow of 40 mL O₂/min, sample mass of 10 mg, and particle size of 30 to 60 mesh (Figure 3).

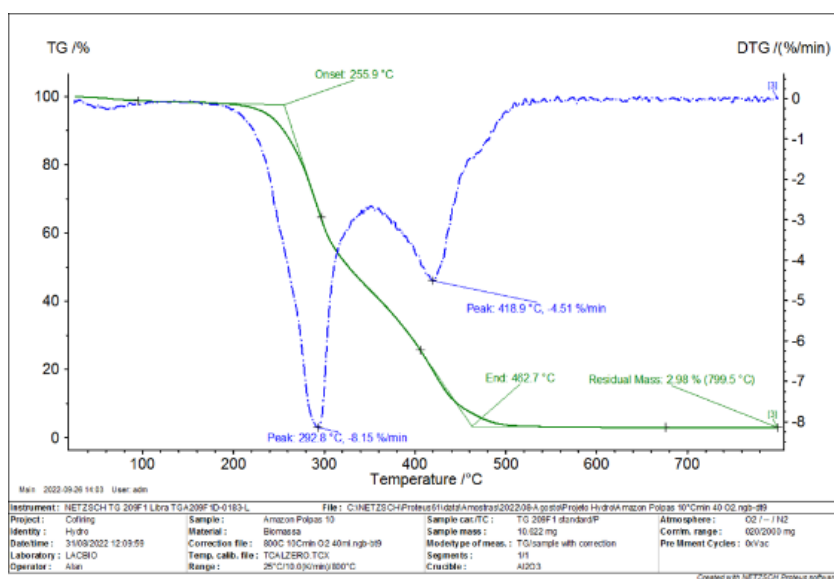


Figure 3. TG Chart, where the green line is mass loss (TG), and the blue line is the time differential thermogravimetry (DTG).

The onset of seed volatilization is above 260 °C, while that of coal is close to 400 °C. The maximum volatilization rate occurs at around 285 °C for the acai seed, while for coal, it is close to 450 °C. The end of volatilization occurs at similar temperatures for both fuels. The conclusion is that biomass starts combustion before coal, and they end almost at the same time [10]. This will represent a bonus for the 100 % biomass-converted boiler once lower temperatures for the acai combustion allow for saving in diesel consumption during boiler start-up operation. There is no risk when handling this biomass in ambient conditions, as the start of its combustion is at a higher temperature.

3.3 Physical Characterization Analysis

A particle size analysis of the acai seed and mineral coal was carried out according to the NBR NM 248 standard. This analysis was done with dry samples in triplicate. Apparent and real density were obtained by adapting the NM-52 standard. For this work, samples of mineral coal and acai seeds were crushed and sieved with a 16-mesh sieve, which is within the range stipulated in the standard. Isopropyl alcohol was also used as a penetrating liquid due to its capillary properties.

It was observed (Table 2) that acai seed has a very uniform distribution, with most of it being retained only in two sieves. Mineral coal has particles bigger than seeds, requiring diameter reduction to facilitate the fluidization process.

Table 2. Particle size distribution for fuels.

Sieve (mm)	Acai seed	Drummond coal
	Retained mass (%)	Retained mass (%)
> 25.00	0.00	7.41
19.00	0.00	3.61
12.50	0.86	8.70
9.50	28.64	7.08
6.30	70.30	9.25
4.76	0.11	9.70
2.36	0.09	11.52
1.18	0.00	15.72
0.60	0.00	13.66
0.30	0.00	8.64
0.15	0.00	3.68
> 0.15	0.00	1.02

The determination of the bulk and true density obtained the results shown in Table 3. It is noted that both fuels have a very similar true density. However, when comparing the bulk density, a large difference is noticed. This fact is due to the natural shape of the acai seed (AS), which has a more spherical shape and causes a greater fraction of voids.

Table 3. Density results for fuels.

	AS with fiber	AS without fiber	Drummond coal
Bulk density (kg/m ³)	376	736	820
True density (kg/m ³)	1 470	1 470	1 400

The lower bulk density of the acai seeds in relation to coal, combined with its lower energy content (heating value), raises a warning regarding the nominal mass and volumetric capacities of the existing transport and storage systems (conveyor belts and boiler silos), which were designed for exclusive operation with coal. Therefore, these data were fundamental for determining the maximum percentage of biomass in the blend to operate safely using all existing systems at Alunorte with no modification until the complete switch from coal to biomass after the boiler conversion project. On the other hand, the existing systems might have to be improved for the new operation from 2030 onwards.

3.4 Ash Analysis

The ash samples' chemical composition was obtained by X-ray Fluorescence Spectrometry (XFS), using a sequential WDS spectrometer, model Axios Minerals from the PANalytical brand, with a ceramic X-ray tube, rhodium anode (Rh), and maximum level of power 2.4 kW.

Ash fusion is one of the bottlenecks for the use of biomass in fluidized bed boilers. If the ash is subjected to temperatures above its melting temperature, it promotes agglomeration of the bed, leading to the destruction of the fluidization of the bed, in addition to other consequences such as corrosion and metal deposition [11].

High silicon and aluminum contents cause the ash melting temperature to be higher, while high potassium and sodium contents cause lower melting temperatures. In fluidized bed boilers, the

melting temperature of the ash must be higher than the bed temperature to avoid the bed agglomeration phenomenon.

Agglomeration occurs when potassium or sodium and silica are present in the fluidization system and form complex compounds such as sodium or potassium silicates with a low melting point (called eutectic mixtures – 770 °C). High alumina contents favor the formation of alkali-aluminum silicates, which have a much higher melting temperature. The presence of sulfur oxides favors the reaction with potassium oxide to form potassium sulfate, which has a higher melting temperature than the eutectic temperature of alkaline silicates [12].

Therefore, it is desirable that the fuel ash has low levels of silica and potassium (or sodium) oxides. However, since these levels are high, agglomeration can be mitigated with significant calcium oxide, aluminum, and sulfur levels. Adding inert agents (kaolin, for instance) can also control this phenomenon.

Table 4 shows that acai seed ash has less silicon than coal (reduction is even greater for seeds without fiber), but potassium content is much higher than in coal and is even higher in the no-fiber seed. The content of the mitigating element, alumina, reduces for the seed without fiber in relation to coal and even more for the seed with fiber. It drives the conclusion that acai seed has a smaller fusion temperature than Drummond coal, and among the acai seeds, the one with fiber is smaller than the fiber-free.

Table 4. Fuels ash composition.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	P ₂ O ₅	CaO	CuO	SO ₃	MgO	TiO ₂	MnO	ZnO	Na ₂ O
Drum. Coal	54.0	23.3	8.7	2.8	0.2	2.4	-	3.7	1.7	1.0	-	-	2.3
AS with fiber	41.2	5.6	3.0	21.3	9.9	7.7	-	4.5	4.3	0.7	1.8	-	-
AS without fiber	16.0	6.8	16.3	27.1	11.0	9.5	-	5.7	4.4	0.5	2.1	0.5	-

Aiming to identify how easily ash starts up the sintering process, ash samples from the three pure fuels were subjected to temperatures ranging from 25–1 000 °C and photographed to identify a reduction in cross-sectional areas, which indicates that the sintering process took place. The sintering process occurs at lower temperature than the melting one [3].

Figure 4 allows us to observe the reduction in the cross-sectional area of each ash sample as a function of temperature. Behaviors such as the presence of cracks and detachment of the sample from the crucible wall were observed. The Drummond coal ash (A) showed signs of cracking at 950 °C and a marked detachment from the crucible wall at 1 000 °C. The fiber seed ash (B) showed signs of detachment at 700 °C with a more pronounced reduction after 850 °C. The fiber-free seed (C) showed signs of cracking and irregular detachment from 900 °C; however, at 950 °C, the signs of reduction are more intense. In short, above 850 °C, the seed with fiber had the greatest reduction in area, followed by the seed without fiber, and the smallest reduction in area was with coal.

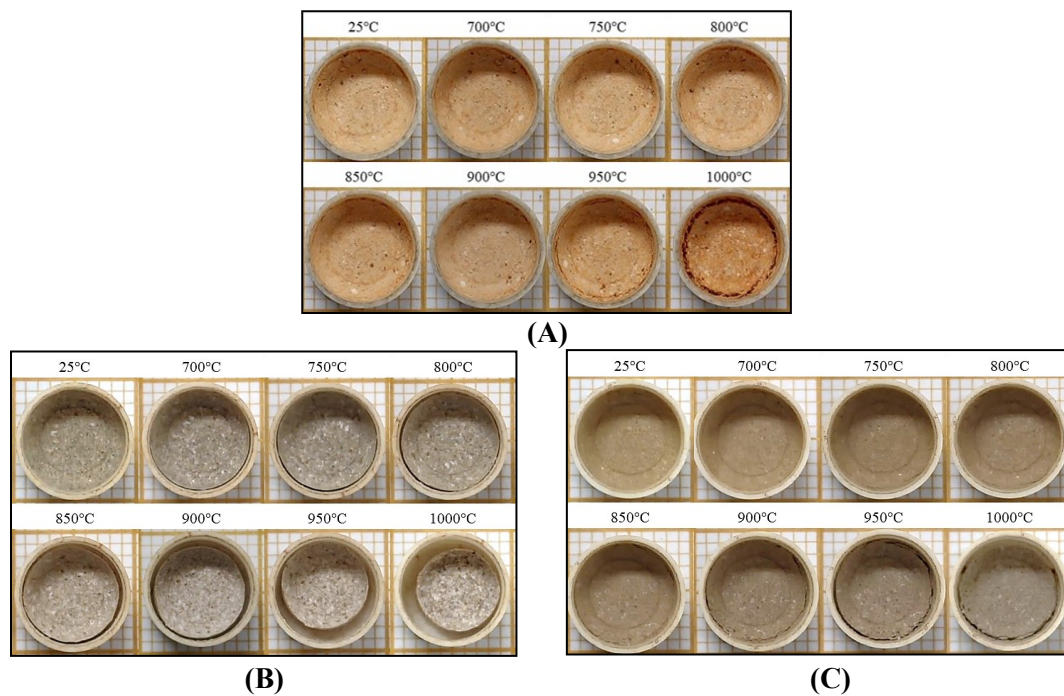


Figure 4. Sintering process visualization. A: Drummond coal, B: acai seed with fiber, C: acai seed fiber-free.

Therefore, it is expected that, with the introduction of biomass into the boiler, the melting temperature of the ash will decrease, as most of the constituent elements of the acai seed ash have the effect of reducing this temperature. This phenomenon was constantly monitored after every step of biomass in the boiler increased during the tests.

4. Co-combustion of Acai Seed and Mineral Coal in BFB Boiler

Two procedures were followed to evaluate the acai seed co-combustion with Drummond coal: a computer simulation considering energy balance and equipment data and industrial tests partially replacing coal for biomass in the BFB boiler [13, 14].

4.1 Computer Simulation of Seed-Coal Co-combustion

This work adopted the computer simulation program CeSFaMB™, which, for its operation, makes use of convergence data, geometry, and equipment operation data, in addition to flow input data [15–18]. It also includes input data on thermochemical properties and chemical characterization of fuels in the Biomass Energy laboratory database at UFPA [5]. In the specific case of the present study, the thermochemical balance was also developed to simulate the combustion process. The simulations carried out were divided into twelve cases, in which temperatures, emissions, and molar fractions were obtained and analyzed [1]. The basic concept of methodology was to keep the amount of inlet energy in the boiler in the reference case as constant. Acai seed LHV is smaller than Drummond coal. Therefore, the same amount of energy requires more mass of seed than coal [1].

The maximum values for replacing coal with biomass were verified considering mainly the following limiting design factors:

- Capacity of primary and secondary air fans: there was no significant variation in these parameters according to simulations comparing the scenarios between 20 % biomass

blend and operation with 100 % coal. The fact that the oxygen content of the acai seed is greater than that of coal – requiring less combustion air – compensates for the need for a greater combustion air flow to burn a greater mass of biomass due to its lower LHV.

- System capacity for transporting and feeding blend: these systems will have to deal with larger volumes of material, given that biomass's heating value per unit volume and bulk density are reasonably lower than those of coal.
- Inventory of inert material in the bed: this is due to the lower content of ash in the biomass. However, in a blend operation with coal, this issue is expected to be insignificant for the boiler operation.
- Ash melting temperature: as discussed in the previous section, elements in acai seeds tend to form compounds with low melting temperatures.

None of these factors represented a bottleneck to the blend operation of up to 20 % biomass in the BFB boiler, showing surplus capacity in the existing equipment. The limiting factor was the transport and storage system.

4.2 Industrial Test: Biomass and Coal Co-combustion in a BFB Boiler

After fuel characterization in the laboratory and combustion simulation modeling, industrial tests of biomass co-combustion with mineral coal were carried out in two bubbling fluidized bed boilers (Alstom A & B), with 20 % being the maximum energy contribution of biomass in replacement to coal. The dosage ramp plan involved the gradual increase of 2.5 absolute points of seed participation in the blend every three weeks, starting at 5 % until 20 %. Ash samples were collected at each level for immediate analysis, XRF, and melting temperature. Isokinetic samples were performed at 10, 15, and 20 % levels. Throughout the test, the operation, maintenance, and engineering teams monitored the boilers' operational parameters in the usual and routine manner.

Before the test, a preliminary phase of up to 5 % seed in the blend (energy basis) was carried out to adjust the new activities related to biomass to the refinery's routine. This phase, called the pre-test, lasted eight months and was extremely important for resolving unforeseen issues, gaining experience, and stabilizing biomass's transport, storage, and dosing activities. Also, before the test, the agreement of the state environmental agency and the knowledge of the refinery's insurance company were obtained. Internally, the management of change was elaborated, involving the participating teams, and a robust risk analysis was performed for the new activities to be carried out.

The acai seed was transported in trucks with loads of approximately 24 t. No stock was formed due to the competition for storage space with coal in the existing sheds. As a result, only enough biomass expected for a day's consumption was received at the refinery. A biomass sample was taken for moisture analysis from each truck.

Exhaust gas composition measurements at the chimney during tests with 10, 15, and 20 % blend of acai seed remained within the limit for the parameters monitored in the chimneys' operational license (particulate matter and SO_x). During the tests, the dosage of limestone remained the same as the operation exclusively with coal. Additional parameters were measured exclusively to carry out the tests to fully comply with the condition of the consent granted by the environmental agency (dioxins, furans, chlorides, fluorides, NO_x, CO, and THC).

The ashes from the blend in industrial tests were subjected to the same analysis described in section 3.4. Up to the level of 17.5 %, it was verified that there was no sign of a reduction in the cross-sectional area, which indicates that the ash samples did not go through the sintering process in the temperature range of 700–1 000°C. For the highest level of biomass blend tested, 20 %,

slight signs of detachment of the sample from the edge of the crucible were observed from 800 °C onwards, as shown in Figure 5. However, this indication becomes more evident only at 1 000 °C. Even so, the reduction in the cross-sectional area was insignificant, indicating that the sample did not go through the sintering process in this temperature range and, therefore, without a tendency to promote bed agglomeration significantly. During routine inspections of the boilers, no points of material deposition resulting from sintering were found inside the equipment.

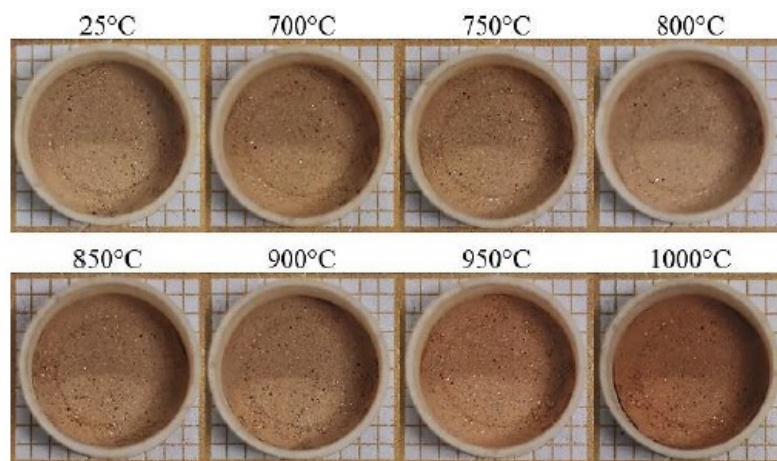


Figure 5. Sintering process visualization for 20 % biomass blend ash in industrial tests.

In short, the industrial tests did not result in operational issues or significant changes in the general behavior of the BFB boilers, indicating that current equipment systems support the use of these biomass fractions well. Preliminary results showed a reduction in the boiler efficiency with the inclusion of biomass; however, this will be evaluated in further detail during the engineering phase for the equipment conversion.

During the 13 months of pre-testing and testing, more than 52 000 t CO₂ was already reduced due to the partial replacement of coal with biomass. With the continuous operation of the blend between 15 and 20 % in the BFB boilers, a reduction of approximately 100 kt of CO₂ annually is expected until they are fully converted to 100 % biomass (in 2030).

5. Conclusions and Further Work

The work carried out along with UFPA has made it possible to verify that Alunorte's current BFB boilers and peripheral equipment can operate with a blend of coal and biomass with a content of at least 20 % in energy input with due safety and operational robustness. Continuous operation with the blend in these boilers over the next few years will be of utmost importance for the continued preparation of the large-scale transformation chain of acai residue into energy biomass. Depending on the maturity of this chain and the availability of this raw material achieved over the next few years, the refinery will be able to definitively convert one or even three coal boilers to exclusively burning biomass by 2030, contributing to the decarbonization goal of 70 % of Alunorte's scope 1 and 2 emissions compared to 2017. With the conversion of one boiler, there is expected to be a reduction of more than 500 kt CO₂ per year in the company's emissions, considering the biomass's share in the energy matrix intended by Alunorte. With the operational continuity of the blend between coal and biomass before the definitive elimination of coal, the potential for CO₂ reduction per year will be around 100 kt.

In addition to continuing the development of the acai residue chain (still incipient in the region) to guarantee reliable supply from 2030 onwards, the following steps of this work include the execution of the industrial test in the CFB boiler and the conversion engineering project of the

boilers and adaptation of peripheral equipment to the renewable fuel. For instance, one of the main challenges that will be solved involves the inventory of inert materials in the BFB boilers and the inventory of fines for the CFB one.

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