

Carbo Culture Final Report

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Introduction:

One of the biggest challenges of the twenty-first century, included in the UN Sustainable Development Goals list, is the need to take action against climate change and rising atmospheric greenhouse gas concentrations.¹ In 2018, Special Report on Global Warming of 1.5 °C published by the Intergovernmental Panel on Climate Change included biochar as a promising negative emissions technology with potential to affect local communities and mitigate the effects of climate change.² Biochar, or biocarbon, is a recognized carbon sequestration method that directly sequesters over three tonnes of CO₂ per tonne of biochar produced. It is also a valuable resource for the agricultural industry as it promotes soil regeneration, plant growth, and improves crop yields.³ Demand for biochar is growing as more farmers and energy companies become aware of its benefits to their soils and energy production at low costs. The global market for biochar is expected to grow at a compound annual growth rate of 16.45% from 2020 to 2025 and reach a global market of 3.5 billion by the end of 2025.⁴

CarboCulture is a biochar-manufacturing startup that aims to remove a gigaton of CO₂ annually by 2030. Their current product stands out on the market due to its high fixed carbon content(>80%), no moisture, low ash (<5%), high cation exchange capacity (100-150 cmol/kg), surface area (more than 300 m²), and conductivity (between 500-2000 mS/cm). The company's biochar production plant includes an air compressor, a Flash Carbonization reactor, and a thermal oxidizer. The process begins with the input of dehydrated, dense waste biomass, sustainably sourced from local partners, such as wood, walnut shells, peach pits, corn cobs, or olive pits. The biowaste is converted into biocarbon during a Flash Carbonization process that also generates a biogas mixture as a byproduct. This mixture of combustible gases is burned in the thermal oxidizer to yield CO₂ and water vapor that are released into the atmosphere. Per a standard batch of 525 kg dried peach pits, biogenic biogas combustion releases 750kWh of energy that is currently being wasted. A life-cycle assessment of the process has shown that the total carbon footprint is 0.195kg CO₂/kg of biochar with 98% of emissions being generated by diesel-powered air compressor operation.

We are seeking to optimize the existing process and further reduce its carbon emissions by utilizing gases leaving the thermal oxidizer at 600°C and 1.5 bar to generate 94 kW of electricity per a standard batch of 525 kg peach pits using an Organic Rankine Cycle and a downstream Cryogenic CO₂ Separation to capture additional 440 kg 99 mol% liquid CO₂ per batch. The ORC module would recover useful waste heat energy from the current process and convert it to electricity available to adjacent plant facilities. Our target is to design the module with high enough generator power output to sustain the operations of currently diesel-run air compressor, second air compressor, and the ORC pump. We would also analyze the feasibility of employing

Cryogenic CO₂ Separation to capture 99% pure CO₂ from the ORC evaporator exhaust. By introducing the separation we hope to achieve sequester even more carbon for the biochar manufacturing process while creating a valuable resource for the chemical industry such as 99% pure liquid CO₂.

The process scope aims to be fitted for a pilot scale version of Carbo Culture's facility, which primarily consists of a 4 meter tall bioreactor and is designed to process biowaste for large farms and other facilities in need of biowaste disposal. Currently, the pilot-scale facility can process up to 800kg of biomass per three hour batches, but frequency of operation varies based on the farms needs or season.

The additions proposed to Carbo Culture's biochar production process begin with a syngas and air mixture entering a thermal oxidizer to be combusted. The syngas mixture is composed of CH₄, CO, H₂, N₂, and CO₂, which leave as byproducts from a flash carbonization reactor. As is, The proposed process will focus on characterizing the desired ORC module and cryogenic separation system. The design choices made for ORC included selection of the working fluid, equipment material, operating temperatures and pressures for each unit as well as the flow rates for optimal heat transfer in condenser and evaporator units. The cryogenic separation design involved similar decisions involving operating pressures, temperatures, material selection, equipment sizing, and optimization for the required product output. To minimize complexity, the project is limited to analyzing only the on-site production and product storage without considering the economics and environmental impacts of post-production selling and transportation.

Before deciding to focus on the ORC and coupled cryogenic separation, alternative processes were proposed for making use of the excess heat and syngas mixture produced by Carbo Culture's current process. For example, using pyrolysis of the biomass to produce a biofuel for future energy use through an alternate production method like HyPR-MEET (Hydrogen Production Multi-staged Enthalpy Extraction Technology) which uses high-temperature steam to oxidize biomass of hazardous waste into hydrogen and energy.⁵ This process produces a higher H₂ content from pyrolysis than ours (around 60 volume % higher) , which is a better energy source than biochar; However, this requires complex mechanical operation, release of CO in bigger than trace amounts, a liquid slag stream, and loss of the useful biochar product.⁵ Since the ORC and cryogenic separation systems proposed will both utilize the biowaste for energy production on-site and help in further sequestering atmospheric carbon into a secure biocarbon product that can be sold off elsewhere, they were the best options to work with.

In addition to the ORC and separation systems proposed here, we suggest a minor change to the equipment CarboCulture currently owns for syngas combustion. We suggest that at this stage of the process, engineering controls and or modifications should be made to look into mitigating

the effects of high temperatures on ceramic insulation that is currently causing cracking on the current oxidizer model.

Plant site:

The current CarboCulture demonstration plant is operating in Central Valley in California adjacent to a walnut processing station. Half of all US produce comes from the Central Valley and the amount of agricultural waste produced annually in the area is estimated to be around 2 million tons. Additionally, there are many forest thinnings and tree removals due to sudden oak deaths and pine beetles in California, producing additional biowaste to be disposed of. These factors account for large amounts of available biowaste feedstock in the region that are provided to the plant free of charge.

Alternative processes:

There are two new modules in our proposed design: an ORC module for waste heat recovery and a cryogenic separation module for Carbon Capture and Storage (CSS). Different heat recovery technologies are available depending on the temperature and quality of the waste heat. For our process, the source of waste heat is the high temperature post-combustion flue gas coming out of the thermal oxidizer at 600°C, so we proposed to utilize it in an Organic Rankine Cycle with an electric generator. One of the alternative waste heat recovery processes that has been demonstrated to be feasible at biochar production facilities is thermoelectric generation.⁶ Thermoelectric generation utilizes the heat directly from biomass pyrolysis, which happens in the combustion unit at 600-800°C. Above the combustion furnace, 13 commercial thermoelectric modules capable of direct heat to electricity conversion are installed. The advantage of such a system is that it is simple, highly portable, and is easy to install and operate. However, the heat recovery efficiency of thermoelectric technologies ranges from 2-5%, which is very low compared to most industrial waste heat recovery systems.⁶ Another disadvantage of this process compared to ours is the small scale at which it is currently optimized to operate. To achieve our design goals, we would need to choose the technology with higher average efficiency and electricity generation capacity that can scale up.

Other methods of waste heat recovery at biochar manufacturing facilities include employing thermodynamic cycles. One viable technology is a heat recovery steam generator (HRSG) connected to a steam turbine that uses waste heat to convert water to steam that can be used for electricity generation. The design of such a system would involve an evaporator, superheater, economiser, steam drum and a steam turbine for power generation. Thermal efficiency of HRSG systems can reach 75-85%.⁷ The disadvantages of the design include large equipment sizing, required on-site operator, high operation and maintenance costs due to turbine corrosion, and lower operational availability compared to ORC.⁸ We chose to implement an ORC module for our process heat recovery since it can operate at lower temperatures and pressures than the conventional steam cycle with similar outputs, has a high efficiency output at part load, has a high degree of automation, and relatively low operating & maintenance costs.⁸

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Figure 1. Process flow diagram from Aspen

Block color	Meaning
	Organic Rankine Cycle (ORC)
	Cryogenic Separation
	Oxidation of pyrolysis gases (designed by Carbo Culture)

Our process begins with an input of a biogas mixture (from the pyrolysis of about 526 kg of peach pits) containing 63.8 weight% (wt%) N_2 , 16.9 wt% CO_2 , 16.1 wt% CO , 2.4 wt% CH_4 , 0.8 wt% H_2 along with air into the thermal oxidizer unit (R1). Catalytic oxidation of the biogenic syngas heats up the reactor chamber to temperatures as high as 600-800°C at which the combustion reactions conversion approaches unity. Thus, we expect the only products coming out of R1 to be CO_2 , water vapor, N_2 , and residual O_2 . A gas-sampling port, a commercial oxygen analyzer, and thermocouples would be installed in the thermal oxidizer to control the operating conditions of the reactor.

The gas mixture leaves the reactor at 600°C to enter the Organic Rankine Cycle. First, hot gas would be used in an evaporator (HX1&H1) to isobarically heat up and vaporize toluene, which we chose as the working fluid due to its demonstrated high thermal decomposition point and total cycle power efficiency (38%).¹³ High-pressure toluene vapor is then expanded in the turbine (T2) that is connected to an electric generator. Work done by isentropic gas expansion in the ORC turbine is found to be 282 kWh per a standard batch. The expanded gas is sent to a constant-pressure condenser (HX2) to be cooled from 224°C to 138°C by a water stream at 25°C, 1 bar from the on-site water pool. After the condenser, liquid toluene is pressurized by the pump to 38 bar and returned back to the evaporator to continue the cycle. Energy balances for each step of the cycle and thermodynamic properties of the working fluid are given in Appendix Ai.

The exhaust flue gas containing CO₂, water vapor, N₂, and O₂ would leave the evaporator at 164°C to enter the cryogenic separation module. Our separation employs the reverse Brayton cycle and is achieved in a series of compression, refrigeration, separation, and cryoenergy recovery steps. First, the flue gas mixture at 164°C containing 14.6 mol% CO₂ is pre-cooled in a multi stream heat exchanger. It is first water-chilled (HX3A) down to 26°C, then additionally chilled by cryogenic reaction products (HX3B) before exiting at 22°C. The exhaust then enters a flash drum H₂O separator (F1) operating at -50°C. Ice will form within this chamber and thaw to liquid between runs, separating the water from other gases. This would prevent ice formation and corrosion later on in the downstream compressors and heat exchangers. The dehydrated gas mixture is compressed to 34 bar (in C2) and passed through a cryogenic heat exchanger (HX4) to cool it to the CO₂ formation point (-80°C at 40 bar). The resulting liquid CO₂ phase is separated in the first CryoSep flash drum separator (F2). The vapor separated out in F2 is sent to an expansion turbine (T4) and sent back to the second heat exchanger (HX4) as a cold stream. The separated CO₂-rich stream is then depressurized from 34 bar to 2 bar by a Joule-Thompson valve and sent to the second separator (F3) to achieve final CO₂ stream purity of 99.8 mol%. The overhead gas from F3 is used as a cold stream in the first heat exchanger (HX3B) and afterwards released into the atmosphere at 25°C. The liquid CO₂ is pressurized by a pump (P2) and heated in HX3B to yield a liquid phase CO₂ product at -43°C, 10 bar. Our design would exploit the thermodynamic properties of CO₂ mixture with air gases. The description of each unit operation is shown in Table 2.

Table 2. Equipment list.

Unit operation (equipment code)	Design Specifications/Assumptions (Volume/Area, P/T, required power)	Descriptions (unit purpose)
Air Compressor (C1)	Axial-flow blower because compression requires minimal energy	Provides compressed O ₂ and N ₂ for the thermal oxidizer
Thermal Oxidizer (R1)	Stainless steel. Catalyst is made of Platinum and palladium supported	Oxidizes exhaust from the biochar production to reduce CH ₄ and CO

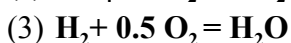
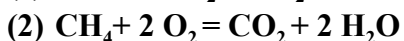
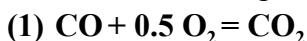
	on a honeycomb monolith disk manufactured from mullite extrudate. Volume of 101 L.	to negligible amounts
ORC Evaporator (HX1 & H1)	Stainless steel and Cu-Ni alloys for shell and tubes of the evaporator. Contact area of 17.5 m ²	Allows heat from the reacting and flue gases to transfer to the ORC working fluid
ORC Turbine (T2)	Back Process Gas turbine made from a Steel/Cu-Ni alloy	Generates electricity from hot toluene vapor
ORC Condenser (HX2)	Made from Steel. Contact area of 6.78 m ²	Uses water at 25°C to cool and condense the turbine exhaust to 138.3°C
ORC Pump (P1)	Low-carbon steel reciprocating positive displacement plunger pump. 12.564 gpm	Increases the pressure of the toluene working fluid
Precooling Heat Exchanger (HX3A & HX3B)	4-stream carbon steel-aluminum coil-wound heat exchanger. Contact area of 10.5 m ²	Pre-cool the flue gas before the separation process using water and separation products to reduce cooling load at the flash separator
Flash Drum Dryer (F1)	Aluminum pressure vessel, a cooling unit, and a demister. Subprocess units are aluminum. Ideal liquid-vapor equilibrium	Separates water from other gases in the ORC exhaust at -50°C
Compressor in Cryogenic Separation (C2)	Cast iron cylinder with a stainless steel piston. 2-stage reciprocating compressor that needs 136.72 kW	Compresses air to 34 bar so that liquid formation is preferred
Phase-Changing Heat Exchanger (HX4)	4-stream brazed aluminum plate-fin heat exchanger. Contact area of 1.52 m ²	Cools expanded flue gas until CO ₂ desublimation temperature at - 80C, 34 bar and separates liquid CO ₂ from other gases.
Separation Turbine (T4)	Low carbon, 3.5% Nickel steel. power production of 26.25 kW	Expands high-pressure exhaust gas to atmospheric pressure to cool it for use in heat exchangers.
1st Flash Drum Separator (F2)	Liquid and vapor are ideally mixed so Raoult's law applies and we have ideal vapor-liquid equilibrium. Pressure vessel is Aluminum	Separates liquid CO ₂ at -80C, 34 bar from an N ₂ -rich gaseous mixture
2nd Flash Drum Separator (F3)	Liquid and vapor are ideally mixed so Raoult's law applies and we have	Separates remaining gaseous impurities from the CO ₂ -rich 2-phase stream at -89.3°C and 2 bar

	ideal vapor-liquid equilibrium. Pressure vessel is Aluminum	
Product Pump (P2)	Assume a minimum product purity of 99.5% CO ₂ . Change in head: 81.6 m, Total head: 102 m. 316 stainless steel rotary pump	Dispenses liquid CO ₂ product at 10 bar at -89°C
Valve (V1)	Aluminum pressure regulating valve	provide additional refrigeration to CO ₂ -enriched 2-phase stream expansion via Joule-Thompson effect from 34 to 2 bar

Detailed design of the thermal oxidizer, R1:

Our main reactor is a PFR catalytic afterburner that oxidizes a gaseous mixture of CH₄, CO, H₂, and CO₂ in a series of independent exothermic combustion reactions. In our Aspen model this corresponds to unit operation R1 (shown in Figures 1 and 2). The purpose of this unit is to utilize the biogenic gases exhausted from a flash carbonization reactor in order to generate heat, which will then be recovered in the downstream Organic Rankine Cycle. A Pd/Pt catalyst is being used to drop the reactor temperature to reduce mechanical constraints and risks for exchanging heat with the organic fluid. The catalyst also allows the reactions to run nearly to completion - this especially benefits CO oxidation, which requires high temperatures to combust fully without a catalyst. Dropping the reaction temperature also reduces formation of N₂O, which is nearly 300 times as impactful as CO₂ on global warming by mass.¹⁴ This technique is used in a variety of industries for scrubbing emissions. The biogenic gas input, when combusted, will turn into carbon dioxide and release excess heat that can be used to further decrease greenhouse gas (GHG) emissions in the production of biochar.

These are a set of combustion reactions that will take place within our thermal oxidizer. In the presence of an oxidizing catalyst, all of the following reactions are approximately first order.



The reactions are limited by the rate of each species adsorption and can be approximated as 1st order when the catalyst is used: $r = k_0 \cdot \exp(-E/RT) \cdot [\text{adsorbate}]$. To find parameters, we used experimental data provided by Carbo Culture and reference values from literature:

- Assume a $k_0 \cdot \exp(-E/RT)$ of 4.0 1/s based on the data for catalytic oxidation of CO and hydrocarbons.¹³ However, this value is an underestimate because it was taken at 573 K, and the steady state temperature of our reaction is around 873 K. We anticipate our reaction rate to be greater by a factor of $\exp(-(1/873) + (1/573))$ or 1.0006. This difference can be considered negligible.

- This leads to a general rate = $4.0 \text{ (1/s)} * [A]$
- Assume an input of 526 kg of peach pits into the FC reactor, then Volumetric flow rate into the thermal oxidizer V'_{in} : 1283.45 L/min
- Necessary mean residence time: $\tau = \sim 1/k = 0.25 \text{ s}$
- Reactor volume: $V = \tau * (V'_{out}) = 101 \text{ L}$

For an input of 526 kg of peach pits in the Flash Carbonization reactor, the thermal oxidizer must be able to hold a flow rate of 399.34 kg/hr or 24247 L/min at the outflow. This is a substantial overshoot due to the higher heat in our reactor model than we expect in our reaction and the fact that the volume increase within the thermal oxidizer is huge. We will assume an approximate $k = 4.0 \text{ 1/s}$ based on the data for catalytic oxidation of CO and hydrocarbons.¹³ From k , we get a residence time of .25 s. Reactor volume is then fixed at $V = \tau * v_0 = 101 \text{ L}$. The catalyst for the reactor is a mixture of platinum and palladium supported on a honeycomb monolith disk manufactured from mullite extrudate. For the reactor, eleven such disks (diameter = 14.3 cm, height = 3.81 cm, density = 3.88 cells/cm²; $V_{cat} = 611.9 \text{ cm}^3$; total for 11 disks $V_{cat} = 6730.9 \text{ cm}^3$) are placed in a galvanized steel cylinder and funnel, wrapped in a ceramic insulator and placed in a steel pressure vessel.¹⁵ According to a US Patent for an energy efficient afterburner that sustains the same temperature as our thermal oxidizer, the ceramic insulator should be 2” thick.¹⁵ The mass and energy balances and process streams around the thermal oxidizer are in Appendix Ai.

Detailed design of flash distillation column, F3

We will use a flash distillation column during the cryogenic separation of CO₂, which is code F3 on our PFD. This unit is responsible for the final purification step, yielding a product with 99.8% purity from a pre-separated high CO₂ stream. The separation is done in two steps because the initial nitrogen content is very high, yielding a substantial fraction in the liquid stream for any reasonable liquid flow rate. These two products have the most similar volatilities and represent the low and high key. In the second flash separator, the partial pressure of CO₂ is much higher with respect to nitrogen, so a greater purity is achieved.

For our model of the flash distillation column shown in Figure 3, we found the mass balances of individual components, energy balance, and Vapor-Liquid Equilibrium (VLE) equations for a mixture of CO₂ and N₂ shown in Appendix Aiii. Our flash drum can be modeled as a distillation column with a single equilibrium stage.

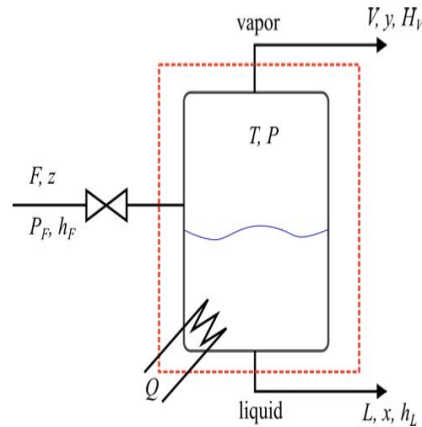


Figure 3. A typical flash drum design

We chose to calculate the diameter of our flash drum distillation column based on the maximum allowable vapor velocity using the Souders-Brown equation:

$$u = (k) \left[\frac{dL - dV}{dV} \right]^{0.5}$$

where:

u is the permissible vapor velocity;

k is the vapor velocity factor = 0.107 m/s

dL is the liquid density = 1277.86 kg/m³

dV is the vapor density = 4.75 kg/m³

We got that $u = 1.7517$ m/s; V = Vapor flow rate = 6048 m³/s; $MW_{vap} = 35.4$ g/mol (from Aspen). Now, we can find the cross-sectional area using $A_c = V \cdot MW_{vap} / (u \cdot 3600 \cdot dV) = 7.07$ m

$$\text{Drum diameter } D = (4 \cdot A_c / \pi)^{0.5}; \quad D = 3 \text{ m}$$

For industrial flash drums, height to diameter ratio (H/D) ranges between 3 - 5 and the optimal value is found by optimizing the vessel cost. Since we are not performing the cost analysis yet, we would set our $H/D = 3$ to find the rest of the sizing parameters. Thus, the total flash drum height $H = 3 \cdot 3 \text{ m} = 9 \text{ m} = h_v + h_L + h_f$, where:

h_v is the height of the drum above the centerline of the feed nozzle

h_L is the the depth of the liquid pool

h_f is the height of the center of the feed line above the maximum level of the liquid pool

We can find the rest of the geometry using:

$$h_L = 4 \cdot V_{surge} / \pi \cdot D^2 \quad \text{where } V_{surge} \text{ is the desired surge volume that can be optimized empirically}$$

$$h_v = 36'' + \frac{1}{2} \cdot d_{feedline} \quad \text{where } d_{feedline} \text{ is the diameter of the feeding nozzle}$$

$$h_f = 12'' + \frac{1}{2} \cdot d_{feedline}$$

We expect $h_L < h_V < h_F$. Since it is established in the industry that $h_F > 48''$ and $h_L > 12''$,¹⁷ d_{feedline} must be greater than 72''.

Process Safety Evaluation

From the feed up to and including the ORC, the main hazards come from the gas exhaust released by the diesel-powered machinery and CO present in the feed stream to the thermal oxidizer and from the high temperatures of the process streams. The equipment must be in a well-ventilated area and gloves and goggles must be worn in the case of spills, leaks, or equipment that isn't well insulated. During the cryogenic separation, the main hazards come from the extremely cold temperatures, gases, and liquids that can cause skin burns if gloves, a face shield, goggles, and protective clothing aren't worn. No skin should be exposed and long-term exposure should be avoided. Staff will be extensively trained in protocol for working with cryogenics and provided with procedures for accident reporting and dealing with leaks or spills. High pressure and cryogenic equipment will be inspected regularly for metal fatigue and will not be used for longer than their qualified lifetime.

Table 3. Plant Safety Assessment

Unit	Equipment	Hazards	Engineering Controls
Compressors	C1, C2	Fumes released from gas-powered machinery, Leaks	Place in a well-ventilated area and use seals. Include automatic relief and emergency shutoff valves. Wear goggles and use gauges to monitor pressure changes.
Pumps	P1, P2	Extremely cold (P2) or hot (P1) temperatures	Include automatic relief and emergency shutoff valves. Keep moving parts guarded. Wear gloves and protective clothing.
Reactors	R1	Toxic fumes, extremely hot temperatures	Ceramic coating to prevent reactor cracking. Temperature sensors and emergency shutoff. Place in a well-ventilated area. Wear goggles, mask, gloves, and protective clothing. Ensure pipes will not leak.
Separation heat exchangers	HX3A, HX3B, HX4	Extremely cold operating conditions. HX4 experiences both hot and cold operating conditions.	Hydrocarbon sensors to detect leaks, potential bypass systems for hot exhaust gas should be

			considered. Place in a well-ventilated area, wear goggles, mask, and protective clothing.
Condenser	HX2	Operating at moderate temperatures, so toluene toxicity is the greatest risk.	Hydrocarbon sensors to detect leaks. Place in a well-ventilated area, wear goggles, mask, and protective clothing.
Evaporator	HX1, H1	Operating at high temperatures. Toluene is both highly flammable, toxic, and a decomposition risk.	Hydrocarbon sensors to detect leaks, potential bypass systems for hot exhaust gas should be considered. Automatic fire suppression equipment should be installed in case of ignition. Place in a well-ventilated area, wear goggles, mask, and protective clothing.
Turbines	T2, T4	Extremely cold (T4) and hot (T2) temperatures, toxic gases	Pressure and temperature sensors coupled with discharge valves. Place in a well-ventilated area and be cautious of leaks. Wear masks, gloves, goggles, and protective clothing and avoid long-term exposure.
Separators	F1, F2, F3	Extremely cold temperatures,	Place in a well-ventilated area. Use of hydrocarbon sensors for monitoring. Prevent CO leaks by properly sealing pipes. Pressure and temperature sensors coupled with discharge valves. Wear masks, gloves, goggles, and protective clothing.

Environmental Considerations:

Carbo Culture follows the methods outlined in Puro.earth's CO₂ removal rules to be considered a net negative carbon emissions technology, the rules needed to earn a European Biochar Certificate (EBC) to be considered a sustainable producer of biochar, and emissions guidelines

outlined by the Clean Air Act. The requirements we must follow are stated as follows and taken from Tables C1 and C2 in Appendix C^{18,19}:

1. Raw biomass input
 - a. The raw biomass input is waste and if it is wood, it is sustainably sourced from a PEFC or FSC certified forest.
 - b. Raw biomass input has guaranteed separation from inorganic matter.
2. Flash Carbonization Reactor (FCR)
 - a. No fossil fuels may be used to heat up the Flash Carbonization Reactor (FCR), unless it is waste heat from another process.
 - b. Gases from the FCR must be recovered and cannot be released.
 - c. At least 70% of the waste heat from the FCR must be used if the annual output is more than 50 tonnes.
 - d. The FCR temperature can only fluctuate 20% above or below the declared pyrolysis temperature.
3. Biochar product
 - a. The biochar must have over 50% stable carbon content as determined by lab tests.
 - b. The end-use of the biochar is not for energy.

Our process releases trace amounts of CO and CH₄, N₂, O₂, and CO₂. The only concern is the release of CO₂ as it is a GHG, and our mitigation strategies are described in the next section. We create a wastewater stream that we recycle until we replace it yearly in order to minimize our water pollution impacts and minimize the buildup of dissolved gases in the water that would affect our equipment as suggested by Carbo Culture.

Pollution Control Strategies:

The addition of an ORC and cryogenic separation to Carbo Culture's biochar production assembly aims to further sequester CO₂ using the combustible gases released in their process. Using a thermal oxidizer reduces carbon monoxide and methane emissions by almost 100%. The heat from this thermal oxidizer was going unused and is now proposed to be used to make energy in the ORC before being exhausted. To further sequester CO₂, the inclusion of a cryogenic separation is used after the ORC. The mass of CO₂ that would have left the ORC unit as exhaust is 820.8 kg/batch (CO₂ flow rate out = 273.6 kg/hr of reactor operation, not normalized). With cryogenic separation module, we would capture 441.6 kg of CO₂ per batch (flow rate out = 147.2 kg/hr). Produced CO₂ is then sold in its liquid form to reduce carbon emissions from the thermal oxidizer off gas by 53.8% (See table C3 in Appendix C). By being a net-negative emissions technology, we only release trace amounts of GHG and thus have a minimal impact on surrounding communities. The plant emits noise pollution while running, but it is located in a rural area far from communities. It could impact the farmers living near the plant, depending on where the plant is located relative to them and how much noise it makes.

Comparison to Bio-oil production

In our process, we use the heat from the pyrolysis to produce energy through an ORC. Other biochar production processes condense the emissions from the pyrolysis to produce bio-oil that can be used as fuel. Bio-oil production from biochar emits 4.05×10^{-2} kg CO₂/MJ of bio-oil produced. When we liquify CO₂, we release around 137 kg CO₂/hr * 3hr = 411 kg CO₂ in exhaust. From the ORC, we produce 119.92 kW * 3 hours = 360 kWh * 3.6 = 1296 MJ. Our process releases 411 kg CO₂ / 1296 MJ produced = 3.17×10^{-2} kg CO₂/MJ of energy produced.²⁰ The production of bio-oil emits more than trace amounts of volatile organic compounds, hazardous air pollutants, nitrogen oxides, and sulfur oxides, and it emits unidentifiable suspended solids into its wastewater.²⁰ Using heat from pyrolysis has less environmental impacts in terms of emissions and water pollution than turning the biochar into bio-oil.

Economic Considerations:

The control volume (CV) for our processes does not include biochar production and sales, so we calculated the cash flow with and without the sale of biochar. For the analysis, we made the following assumptions:

1. Based on an economic analysis of biochar production plants, we can claim depreciation allowances for seven years, and the depreciation of our equipment can best be characterized by the variable declining balance method.²¹
2. For depreciation, the salvage value of our equipment can be calculated by the following formula:

$$\text{Salvage value} = \text{Initial cost} * (1 - \text{number of years used/number of service years})^{22}$$

We will assume pumps and turbines have 17 service years, carbon steel pipes have 18 service years, and other equipment has 20 service years.²³ We will also assume we cannot claim depreciation on equipment already purchased, which is the flash carbonization reactor and air compressor C1.

3. We will pay state taxes in California at a flat rate of 8.84% a year.²⁵
4. We can subtract the total depreciation of all our equipment from our taxable income to determine what tax bracket we will fall in for federal taxes. We will pay federal taxes according to the following table:²⁴

Table 4. Federal income tax brackets and rates.

Tax rate	Taxable income bracket	Tax owed
10%	\$0 to \$9,875	10% of taxable income
12%	\$9,876 to \$40,125	\$987.50 plus 12% of the amount over \$9,875
22%	\$40,126 to \$85,525	\$4,617.50 plus 22% of the amount over \$40,125
24%	\$85,526 to \$163,300	\$14,605.50 plus 24% of the amount over \$85,525
32%	\$163,301 to \$207,350	\$33,271.50 plus 32% of the amount over \$163,300
35%	\$207,351 to \$518,400	\$47,367.50 plus 35% of the amount over \$207,350

5. We will assume an inflation rate of 2.5%²¹

The costs of our plant are summarized below and described in further detail in Appendix Bi through iii:

Table 5. Costs of the plant.

Total Capital Cost (all equipment, piping, and labor costs for manufacturing)	\$2,389,123.05
Variable cost of production (from electricity, water, and the thermal oxidizer catalyst)	\$54,108.88/year
Fixed cost of production (from insurance and maintenance)	\$50,528.17/year

We will have to pay federal and CA state taxes yearly. To determine our tax bracket, we must take depreciation into account for seven years after our plant operates for one year and subtract it from our income. Our income sources come from liquid CO₂ sales (when we are within the CV),

biochar sales, and selling carbon credits that we earn but cannot use ourselves due to the small size of our plant.

We will not have to pay taxes for environmental protection, but we earn carbon credits we cannot claim because we don't qualify at our current plant size.²⁶ We currently sell our tax credits to Puro.earth for \$100/ton of biochar produced and each ton of biochar we make yields 3.2 carbon credits. Since we make 118.06 tons of biochar/year, we earn 377.792 carbon credits a year that we sell for \$37,700.79/year. Each ton of liquid CO₂ sequestered should yield 1 carbon credit, and we produce 497.22 tons annually. This leads to \$47,224.63/year in additional earnings.

Our sources of revenue are described below in Table 6. All sources are taxable income at the state and federal level.²⁷:

Table 6. Revenue sources for Carbo Culture

Source of revenue	Yearly sales
Liquid CO ₂ (within CV of this report)	\$86,506.20
Liquid CO ₂ Carbon Credit (within CV of this report)	\$49,724.63
Biochar (outside CV of this report)	\$304,164
Biochar Carbon Credit (outside CV of this report)	\$37,700.79

The total depreciation of all our equipment is \$36,786.86, which puts us at the 35% tax bracket when we include biochar sales and 22% tax bracket when we stay within the CV when we can claim depreciation. When we can't claim depreciation, we will be in the 35% tax bracket when we include biochar sales and 24% tax bracket when we stay within the CV. More data on our depreciation, costs, and tax calculations is shown in Appendix Bi through Biii and in the attached excel sheet.

To calculate the pre-tax ROI, we will use the formula below:

$$\text{Pre-tax ROI} = \text{Average Annual Cash Flow} / \text{Total Investment required}$$

When we stay within the CV of this report, the average annual cash flow across 25 years is \$36,821.95, and the pre-tax ROI is \$0.01. When we include biochar sales, the average annual cash flow across 25 years is \$378,686, and the pre-tax ROI is \$0.15. The calculations are in the attached excel sheet titled Cash Flow Calculations.

The cash flow table within the CV is below:

Table 7. Cash flow diagram within the CV

Cash flow within CV										
Year	Income	Net income	Federal tax	CA state tax	Operating costs	Fixed Costs	Nominal cash flow	Real cash flow	Real Cumulative cash flow	Notes
1	136230.83	136230.83	\$26,774.90	12042.80537	2525043.445	45300	(\$2,472,930.32)	(\$2,472,930.32)	(\$2,472,930.32)	Operating costs include TCI
2	136230.83	\$86,724.91	\$14,869.48	7666.482188	54108.88	45300	\$14,285.99	\$13,597.61	(\$2,459,332.71)	Claim depreciation
3	136230.83	\$86,724.91	\$14,869.48	7666.482188	54108.88	45300	\$14,285.99	\$13,265.96	(\$2,446,066.75)	Claim depreciation
4	136230.83	\$86,724.91	\$14,869.48	7666.482188	54108.88	45300	\$14,285.99	\$12,942.40	(\$2,433,124.35)	Claim depreciation
5	136230.83	\$86,724.91	\$14,869.48	7666.482188	54108.88	45300	\$14,285.99	\$12,626.73	(\$2,420,497.62)	Claim depreciation
6	136230.83	\$86,724.91	\$14,869.48	7666.482188	54108.88	45300	\$14,285.99	\$12,318.76	(\$2,408,178.86)	Claim depreciation
7	136230.83	\$86,724.91	\$14,869.48	7666.482188	54108.88	45300	\$14,285.99	\$12,018.30	(\$2,396,160.56)	Claim depreciation
8	136230.83	\$86,724.91	\$14,869.48	7666.482188	54108.88	45300	\$14,285.99	\$11,725.18	(\$2,384,435.38)	Claim depreciation
9	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,598.06)	(\$2,386,033.44)	
10	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,559.08)	(\$2,387,592.52)	
11	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,521.05)	(\$2,389,113.57)	
12	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,483.96)	(\$2,390,597.53)	
13	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,447.76)	(\$2,392,045.29)	
14	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,412.45)	(\$2,393,457.74)	
15	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,378.00)	(\$2,394,835.74)	
16	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,344.39)	(\$2,396,180.13)	
17	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,311.60)	(\$2,397,491.73)	
18	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,279.61)	(\$2,398,771.34)	
19	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,248.40)	(\$2,400,019.74)	
20	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,217.95)	(\$2,401,237.69)	
21	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,188.24)	(\$2,402,425.93)	
22	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,159.26)	(\$2,403,585.20)	
23	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,130.99)	(\$2,404,716.18)	
24	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,103.40)	(\$2,405,819.59)	
25	136230.83	136230.83	\$26,774.90	12042.80537	54108.88	45300	(\$1,995.75)	(\$1,076.49)	(\$2,406,896.08)	

The cash flow table when we include biochar sales is below:

Table 8. Total cash flow of Carbo Culture with our proposed changes.

Cash flow with biochar										
Year	Income	Net income	Federal taxes	CA state tax	Operating costs	Fixed Costs	Nominal cash flow	Real cash flow	Real cumulative cash flow	Notes
1	478095.62	478095.62	\$142,127.97	42263.65281	2525043.445	45300	(\$2,276,639.44)	(\$2,276,639.44)	(\$2,276,639.44)	Operating costs include TCI
2	478095.62	\$428,589.70	\$124,800.90	37887.32962	54108.88	45300	\$215,998.51	\$205,590.50	(\$2,071,048.95)	Claim depreciation
3	478095.62	\$428,589.70	\$124,800.90	37887.32962	54108.88	45300	\$215,998.51	\$200,576.09	(\$1,870,472.86)	Claim depreciation
4	478095.62	\$478,095.62	\$142,127.97	42263.65281	54108.88	45300	\$194,295.12	\$176,021.79	(\$1,694,451.07)	Claim depreciation
5	478095.62	\$478,095.62	\$142,127.97	42263.65281	54108.88	45300	\$194,295.12	\$171,728.58	(\$1,522,722.49)	Claim depreciation
6	478095.62	\$478,095.62	\$142,127.97	42263.65281	54108.88	45300	\$194,295.12	\$167,540.07	(\$1,355,182.42)	Claim depreciation
7	478095.62	\$478,095.62	\$142,127.97	42263.65281	54108.88	45300	\$194,295.12	\$163,453.73	(\$1,191,728.69)	Claim depreciation
8	478095.62	\$478,095.62	\$142,127.97	42263.65281	54108.88	45300	\$194,295.12	\$159,467.05	(\$1,032,261.63)	Claim depreciation
9	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$180,079.02	(\$852,182.62)	
10	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$175,686.85	(\$676,495.77)	
11	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$171,401.80	(\$505,093.97)	
12	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$167,221.27	(\$337,872.70)	
13	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$163,142.70	(\$174,730.00)	
14	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$159,163.61	(\$15,566.38)	
15	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$155,281.57	\$139,715.19	
16	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$151,494.22	\$291,209.41	
17	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$147,799.24	\$439,008.64	
18	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$144,194.38	\$583,203.02	
19	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$140,677.44	\$723,880.46	
20	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$137,246.28	\$861,126.75	
21	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$133,898.81	\$995,025.56	
22	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$130,632.99	\$1,125,658.55	
23	478095.62	\$478,095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$127,446.82	\$1,253,105.37	
24	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$124,338.36	\$1,377,443.73	
25	478095.62	478095.62	\$111,529.07	42263.65281	54108.88	45300	\$224,894.02	\$121,305.72	\$1,498,749.44	

Within the CV of this report, where the only source of revenue is from liquid CO₂ sales and sales of its carbon credits, the cash flow diagram is shown in Figure 4.

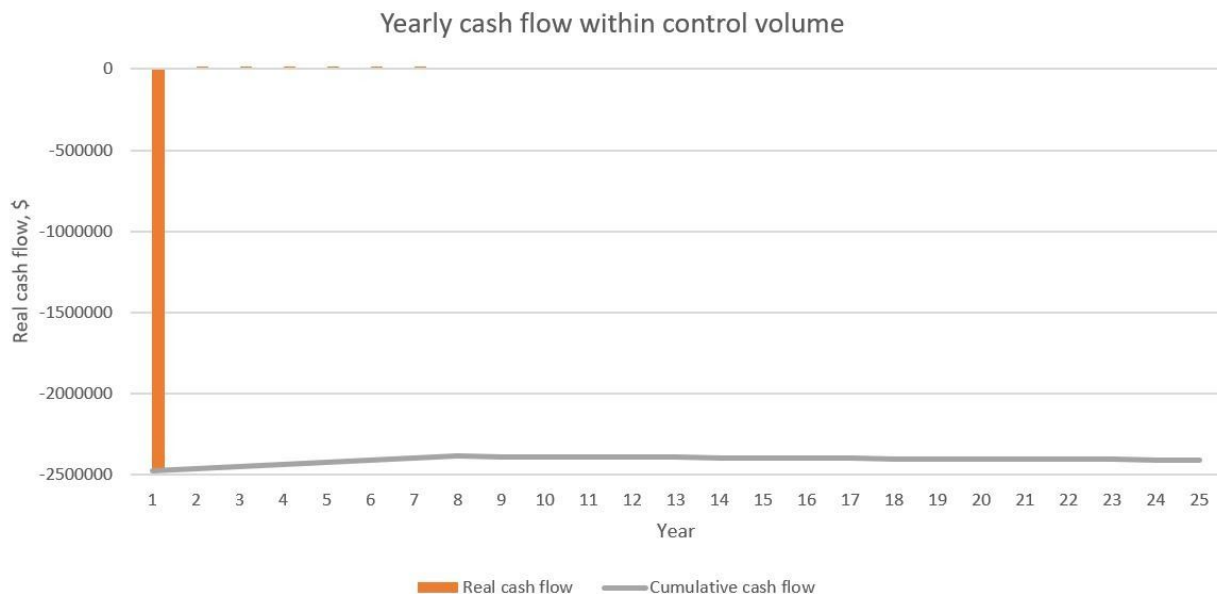


Figure 4. The yearly cash flow within the control volume. Cash flow is adjusted for inflation.

Figure 5 below shows the yearly cash flow throughout the lifetime of the plant if we take the sales of biochar into account. We assume that we will not need to pay for the flash carbonization reactor since it is already in operation and that we cannot claim depreciation on the flash carbonization reactor. We will break even in between the 14th and 15th year of operation.

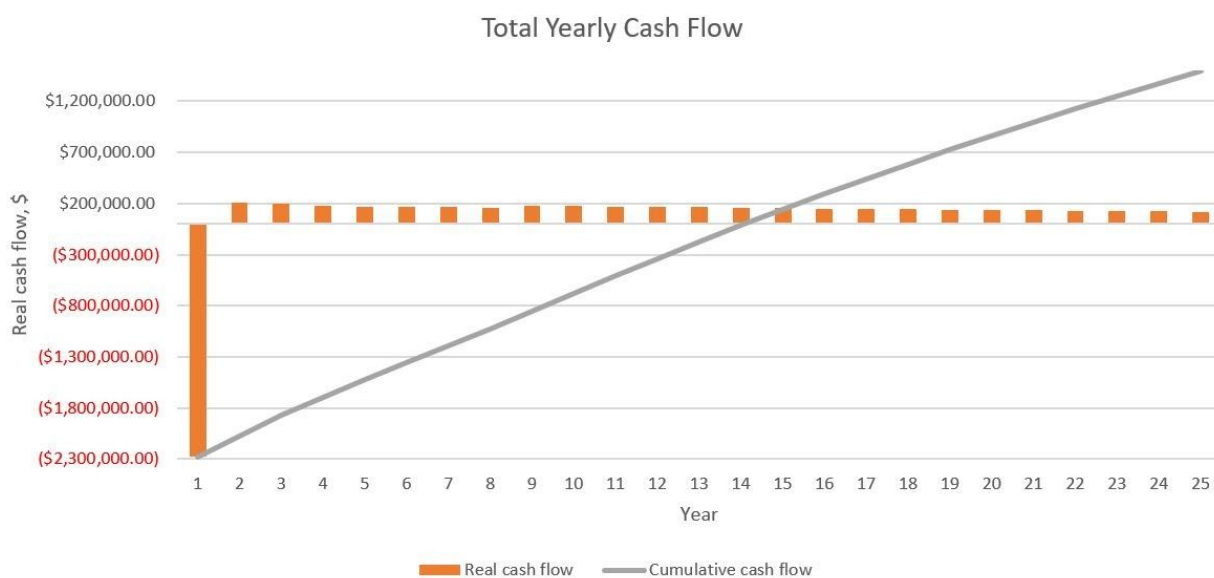


Figure 5. Yearly cash flow when all sources of revenue described in Table 6 are taken into account and taxes are adjusted accordingly.

We saved energy costs since we have the thermal oxidizer's excess heat be the sole source of energy for the air compressor, which reduces economic costs and the carbon footprint of the whole process.

Additionally, we cut costs of the water we use for cryogenic separation and the ORC. We will use a pool that contains enough water for two batches and replace it yearly.

For final design of the biochar production plant, the value of CO₂ separation and sales should be questioned. As seen in the CV cash flow diagram, the costs of maintaining the process continuously outweigh the sales. The biochar production plant would be more profitable if we add only an ORC after the thermal oxidizer, because the energy produced would power the air compressor and the rest would be sold back to the grid and the maintenance, insurance, and equipment costs would decrease significantly.

Conclusion:

Our overall process consists of three major subprocesses: reaction of the produced syngas, energy recapture, and separation and purification of CO₂. Of these modules, the second two are new additions, while the first is a modification to Carbo Culture's existing infrastructure. However, it is evident that the two added phases of processing are unequal in terms of operating and capital costs. Our ORC addition successfully covers the electrical costs of the compressor for the thermal oxidizer, utilizes the thermal oxidizer exhaust instead of having it released, and allows energy to be sold to the grid or used onsite for flash carbonization. As seen by our economic analysis, the cryogenic separation for the sale of CO₂ has a net loss due to the extensive equipment and maintenance required to make a pure liquid CO₂ product. Not enough liquid CO₂ is created from the current batch size of biomass to make the process profitable, but if the process is scaled up the cryogenic separation may become a value addition. At higher flow rates, the equipment cost is proportionally smaller and additional tax breaks are available. This effect can be magnified if multiple batch flash carbonization reactors at the current scale or larger feed into a single separation system to achieve more continuous operation. It is in Carbo Culture's best interest to adopt the ORC addition at their current pilot scale, because it decreases CO₂ emissions by 119 kg assuming 70% of the heat is recovered from the thermal oxidizer as suggested by Carbo Culture. Decreasing total carbon emissions could lead to utilization of carbon credits to further decrease costs across the process as a whole, which would be useful when the process scales up enough to be eligible for tax credit.

Moving forward, Carbo Culture should continue to optimize the ORC. Our current system is designed based on a mix of single variable optimization and numbers from past research, but a comprehensive multivariable optimization could greatly boost the overall ORC efficiency. More analysis should also be done of the time variant startup and shut down behaviors. It may be preferred to vary pressure at the beginning and end of operation as mass flow rates of exhaust change and/or vary the mass flow rate of toluene.

Carbo Culture is also planning to scale up their facility in the near future. Running an analysis of the ROI of these additions at a variety of scales could aid in their choice of future facility size.

Appendix A Process streams and balances

I. Thermal Oxidizer Process Streams:

Compound	Flow rate into thermal oxidizer (kmol/hr)	Initial concentration (mol/L)	Initial reaction rate	Expected behavior
H ₂	2.128	0.0066	rate = 4.0* [CO] .0264 mol/L*s	Reaction rate will decrease as reaction progresses
CO	3.288	0.01	rate = 4.0* [CH ₄] .04 mol/L*s	Reaction rate will decrease as reaction progresses
CH ₄	0.86	0.0027	rate = 4.0* [H ₂] .0108 mol/L*s	Reaction rate will decrease as reaction progresses

Table A1. Reaction rates in thermal oxidizer.

Stream Component (Aspen label, direction)	Amount (kmol/hr)	Enthalpy (Sensible)* (kJ/kmol)	Enthalpy (Formation) (kJ/kmol)	Energy contribution (kJ/hr)
H ₂ (FEED, in)	2.1282	0	0	0
N ₂ (FEED, in)	13.02	0	0	0
CO (FEED, in)	3.29	0	-110527	-363634
CO ₂ (FEED, in)	2.19	0	-393522	-861813
CH ₄ (FEED, in)	0.86	0	-74850	-64371
O ₂ (2, in)	4.72	1439	0	6792
N ₂ (2, in)	18.9	1420	0	26838
H ₂ O (3, out)	3.73	2529	-241826	892578
O ₂ (3, out)	0.435	2217	0	-964
N ₂ (3, out)	31.9	2182	0	-69606
CO ₂ (3, out)	6.22	2905	-393522	2429638
Total				1995458

Table A2. Energy balance around thermal oxidizer.

Stream	Reactor Inlet (FEED, biogas)	Reactor Inlet (#2, air)	Reactor Outlet (Aspen)
Temperature (C)	600	73.9	600

Pressure (bar)	4.83	1.5	1.5
Volumetric flow rate (L/min)	5395.8	7570.4	34280.4
Molar flow rate (kmol/hr)	21.5	23.6	42.5
Mass flow rate (kg/hr)	571.5	680.4	1251.9
Composition (mol%)	H2: 9.9% N2: 60.6% CO: 15.3% CO2: 10.2% CH4: 4% H2O: 0%	N2: 80% O2: 20%	N2: 75.13% O2: 1% CO2: 14.63% H2O: 8.8% CH4: trace CO: trace H2: trace
Hazards	Flammable	Minimal (Moderate pressure and temperature)	Hot Toxic to inhale - high CO %

Table A3. Properties and hazards of the process streams surrounding the thermal oxidizer.

Stream	Description	Direction	Total mass flow (kg/hr)	Enthalpy flow (kW)
FEED	Syngas from flash carbonization	In	571.5	-246.3
AIR	Air from surroundings	In	680.4	9.32
3	Combusted and cooled gases	Out	1251.9	-709
Net heat from combustion				-945.98

Table A4. Mass and energy transport through streams around thermal oxidizer (R1)

II. Thermal oxidizer mass and energy balances

Mass and Energy Balances by hand (CV around thermal oxidizer)

- Releases .00089 kg Co₂e / m³ waste gas treated²⁸
- Assume full conversion of CO, CH₄, H₂ into CO₂ and H₂O for energy calculations
- Assume negligible changes in kinetic and potential energies; no shaft work/moving parts (W=0) for EB

Mass balance:

$$\begin{aligned}
 m_{gas,in} + m_{air,in} - m_{ext,out} &= m(gen_{CO_2}) + m(gen_{H_2O}) - m(cons_{CO}) - m(cons_{CH_4}) - m(cons_{O_2}) \\
 m_{gas,in} &= m_{CO,in} + m_{CH_4,in} + m_{CO_2,in} + m_{N_2,in} + m_{H_2O,in} \\
 m_{air,in} &= m_{O_2,in} + m_{N_2,in} \\
 m_{ext,out} &= m_{CO_2,out} + m_{H_2O,out} + m_{N_2,out} + m_{O_2,out}
 \end{aligned}$$

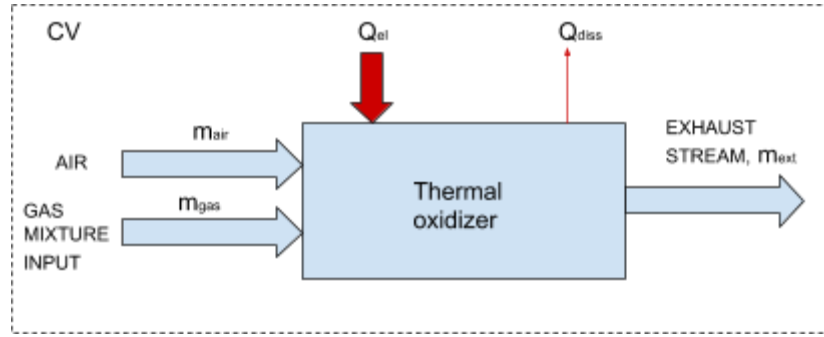


Figure A1. Block flow diagram of the thermal oxidizer to show boundaries of energy balance.

Energy balance for the reactor:

$$\begin{aligned}
 \sum m_{in} h_{in} - \sum m_{out} h_{out} - \sum Q + \sum W &= dU/dt \\
 (m_{CO,in} h_{CO,in} + m_{CO_2,in} h_{CO_2,in} + m_{CH_4,in} h_{CH_4,in} + m_{H_2,in} h_{H_2,in} + m_{air,in} h_{air,in}) - (m_{CO_2,out} h_{CO_2,out} + \\
 m_{H_2O,out} h_{H_2O,out} + m_{air,out} h_{air,out}) + Q_{el} - Q_{diss} + W &= dU/dt = Q_{usable}
 \end{aligned}$$

Catalyst heater electricity consumption: $Q_{el} = 2 \text{ kWh/batch}$; $Q_{diss} = \text{heat loss}$;

$$Q_{net} = \sum m_{in} h_{in} - \sum m_{out} h_{out} = 4701.6 \text{ kW} \quad \text{where } Q_{net} = Q_{usable} - Q_{el} + Q_{diss}$$

Q_{usable} is equal to the total energy available as heat. A fraction of this will be recovered by the ORC. This balance assumes that every reaction goes to completion unlike the Aspen model. The actual energy generated by the reaction will likely fall somewhere between the two.

III. Material and energy balances for the 1st CryoSep flash column (F2)

Assumptions:

- Liquid and vapor are ideally mixed so Raoult's law applies. This is valid since pressure is low (2 bar) and CO_2 and N_2 are molecularly similar
- Uniform pressure and temperature in the flash drum
- Ideal vapor-liquid equilibrium in the flash drum
- Assume a binary mixture of CO_2 and N_2 since other compounds comprise negligible amount (0.3mol%) of the input stream into the flash drum
- Peng-Robinson Equation of state for thermodynamic calculations

- Minimum product purity of 99.5% CO₂
- Assume steady state for the overall process

For the flash equilibrium calculations, we used the Rachford-Rice equation (shown below in Figure 6), where

z_i is the mole fraction of i in the feed stream

β is the fraction of feed that is vaporised

K_i is the vapor to liquid mass transfer equilibrium constant of i

$$\sum_i \frac{z_i (K_i - 1)}{1 + \beta (K_i - 1)} = 0$$

Figure A2. Rachford-Rice equation

K_i is found using Raoult's law (shown below in Figure 7). $K_i = y_i/x_i$ where x_i/y_i - liquid/vapor fraction of i at equilibrium. Since the equation can have multiple solutions for β , our constraint is $x_{\text{CO}_2} > 0.99$ which is the desired product purity.

$$x_i = \frac{z_i}{1 + \beta(K_i - 1)} \quad K_i = \frac{y_i}{x_i} = \frac{P_i^{\text{sat}}}{P}$$

$$y_i = K_i x_i.$$

Figure A3. The application of Raoult's law to find equilibrium constants

Flash calculations using Raoult's law are summarized in Table A5, the material and energy balances are listed alongside it, and the phase diagrams for a CO₂-N₂ mixture under the flash drum's conditions are shown below in Figures A6 and A7:

component	CO ₂	N ₂
Tc (K)	304,1	126,2
Pc (MPa)	7,37	3,39
omega	0,239	0,039
P ^{sat} _i (MPa)	0,09646138	19,63862161
K _i	0,48230688	98,19310805
1-K _i	0,51769312	-97,1931081
z _i	0,9	0,1
D _i	0,48605395	-1,10755714

Table A5. Calculations of CO₂ and N₂ properties in the flash drum.

Material & Energy balance:

$$F = L + V; Fz_i = Lx_i + Vy_i$$

$$F \cdot h_F + Q = L \cdot h_L + V \cdot h_v$$

where F/L/V is the feed/liquid/vapor mass flow rate respectively, i is the component (N_2 or CO_2), h_i is the enthalpy of the stream

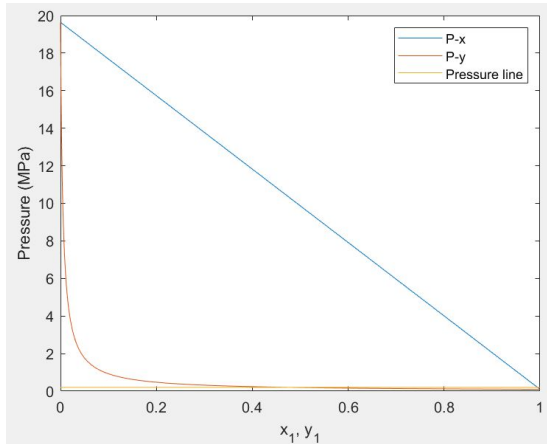
Phase diagrams:

Figure A6: P-x-y curve at -89.8°C

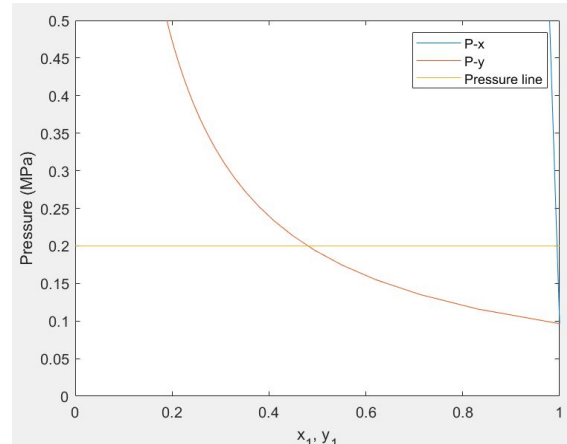


Figure A7: P-x-y curve in the region of interest

IV. ORC Process Streams:

Chemical Formula	Mass flow rate in every ORC stream (kg/hr)	MW (kg/mol)	T_{crit} (°C)	P_{crit}	Boiling Point(°C)	E_{evap} (kJ/kg)
C_7H_8	4146	0.092	318.65	41.06	110.7	365.0

Table A6. Thermophysical properties of toluene as the working fluid²⁹

ORC Evaporator (HX1&H1) energy balance: $\sum m_{in} h_{in} - \sum m_{out} h_{out} - \sum Q + \sum W = dU/dt, VdP=0$
(isobaric heat addition process) $\rightarrow dQ=dH$

Net heat added to the working fluid: $Q_{add} = H_{ORC2} - H_{ORC5} = 1062.15 - 416.8 = 645kW$

Heat released or absorbed by each stream can be found using $\Delta H = \sum m_i C_{p,i} \Delta T$

Stream Aspen Label	Description	Direction	Total mass flow (kg/hr)	Heat Capacity Cp (J/kg*K)	Enthalpy flow (kW)
3	Hot thermal oxidizer exhaust gas	In	1252	1209.4	-709

ORC5	Toluene liquid	In	4146	2082.9	416.8
Exhaust	Cooled flue gas	Out	1252	1081.5	-882.4
ORC2	Toluene vapor	Out	4146	4966.3	1062.15
Net heat					-112.45

Table A7. Energy balance around ORC Evaporator

Work done by the ORC Turbine: $W_T = H_{ORC3} - H_{ORC2} = 968.52 - 1062.15 = -93.67 \text{ kW}$ (*Electricity output*)

Heat rejected in the ORC Condenser: $Q_{cond} = H_{ORC3} - H_{ORC4} = 968.52 - 400 = 568.52 \text{ kW}$

Work done by the ORC Pump: $W_T = H_{ORC5} - H_{ORC4} = 416.8 - 400 = 16.8 \text{ kW}$ (*Pump power req.*)

Stream Aspen label	Description, P and T	Volumetric flow rate (L/s)	Total mass flow (kg/hr)	Mass Enthalpy (kJ/kg)	Enthalpy flow (kW)
ORC2	Toluene vapor 38 bar, 317°C	7.28	4146	922.2	1062.15
ORC3	Expanded toluene vapor 2 bar, 224°C	249.8	4146	840.88	968.52
ORC4	Condensed toluene 2 bar, 138°C	1.53	4146	347.25	400
ORC5	Pressurized toluene liquid 38 bar, 144°C	1.55	4146	361.86	416.8

Table A8. ORC process streams information

V. CryoSep Process Streams:

Stream Aspen label	Description, P and T	Direction	Volumetric flow rate (L/s)	Total mass flow (kg/hr)	Mass Enthalpy (kJ/kg)	Enthalpy flow (kW)
Exhaust	Flue gas leaving ORC evaporator,	In	286.1	1251.9	-2537.3	-882.4
W3	Water for cooling, 1 bar, 25°C	In	1	3603	-15972.1	-15985.6
S9	Pressurized CO ₂	In	0.032	147.41	-9409.2	-385.3
G1	2nd flash separator	In	0.707	12.1	-5251.5	-17.65

	overhead, 2 bar, -89.5°C					
S2	Cool flue gas leaving the HX3, 1.5bar, 22°C	Out	178.5	1251.9	-2804.6	-975.3
W4	Heated water, 1 bar, 44.7°C	Out	1.03	3603	-15882.8	-15986.3
PRODUC T	Liquid CO ₂ , 10 bar, -42.6 °C	Out	0.0365	147.4	-9329.6	-382
G2	Exhaust gas stream, 2 bar, 25°C	Out	1.17	12.1	-5148.53	-17.3

Table A9. Energy balance around precooler (HX3A&HX3B)

IV. All Process Streams:

See attached excel document (AllStreams.xlsx)

Appendix B, Economic Analysis

I. TCI calculation

To calculate the Total Capital Investment (TCI) of the plant, we used the formula shown below:

$$\text{TCI} = \text{ISBL} + \text{OSBL} + \text{Contingency}$$

ISBL: Inside battery limits plant cost, includes all process equipment, piping (40% of process equipment)^F, labor and installation costs (50.49% of process equipment cost), and engineering and supervision costs (22.95% of process equipment cost)

OSBL: Outside battery limits plant cost, assumed to be 40% of the ISBL

Contingency costs: assumed to be 8% of the ISBL

Percentages for assumptions determined by the Chemical Engineering Plant Index

ISBL = Equipment costs + piping + labor and installation + engineering and supervision

ISBL = \$782,385 + \$312,954 + \$395,026.19 + \$179,557.36 = \$1,669,922.54

Equipment costs:

UNIT OPERATION (PFD CODE)	ESTIMATED COSTS
Compressor in Cryogenic Separation (C2)	\$61,793
ORC Pump (P1)	\$2,500
Product Pump (P2)	\$6,469
ORC Evaporator (HX1 & H1)	\$25,193
ORC Turbine (T2)	\$262,101

ORC Condenser (HX2)	\$12,827
Flash Drum Dryer (F1)	\$367,271
Precooling Heat Exchanger (HX3A & HX3B)	\$10,470
Phase Changing Heat Exchanger (HX4)	\$2,663
1st Flash Drum Separator (F2)	\$6,468
2nd Separation Turbine (T4)	\$21,200
2nd Flash Drum Separator (F3)	\$230
Valve (V1)	\$200
Liquid CO₂ Storage	\$3,000
Total Costs:	\$782,385

Table B1. Costs of equipment needed.

Details of equipment costs are shown in the attached excel sheet, Cash Flow Calculations.

$$\text{OSBL} = .40 * \$1,669,922.54 = \$667,969.02$$

$$\text{Contingency} = .08 * \$1,669,922.54 = \$133,593.80$$

$$\text{TCI} = \$1,669,922.54 + \$667,969.02 + \$133,593.80 = \$2,471,485.37$$

II. Variable cost of production calculation

The variable costs of production include the cost of the catalyst, water, and electricity.

Catalyst:

The thermal oxidizer uses 11 catalyst disks at \$199.99 per disk for a total of \$2199.89.²⁹

Catalyst must be replaced after about 12000 hours of operation.³⁰

The hourly catalyst cost is 0.18 \$/hr.

Electricity:

Electricity consumption	Cost	Usage	Total usage
<ul style="list-style-type: none"> Air Compressor (C1) CryoSep Compressor (C2) ORC Pump (P1) Product Pump (P2) ThOx Catalyst Heater CryoSep Pre-Cooling 	16.7c per kWh	<ul style="list-style-type: none"> 9.37 kW 136.72 kW 16.84 kW 0.09 kW 0.67 kW 52.80 kW 	216.49 kW
Electricity production on site		Quantity	Total production

<ul style="list-style-type: none"> • ORC turbine (T2) • Exhaust turbine (T4) 		<ul style="list-style-type: none"> • 93.67 kW • 26.25 kW 	119.92 kW
Net electricity demand from the grid			96.59 kW Cost: 16.13 \$/hr

Table B2. Electricity demand and consumption**Water**

Water is recycled through the process. The water produced by our process is used to replenish lost or evaporated water. The water will be replaced entirely once per year.

Water	Cost	Usage	Size of water pool	Annual cost
<ul style="list-style-type: none"> • ORC Cooling water • CryoSep Cooling water 	0.069 \$/kg	9785.6 kg/hr 360 kg/hr	Water pool will hold enough water for 2 batches. $10,145.60 \text{ kg/hr} * 6 \text{ hr} = 60,873.6 \text{ kg}$	\$4,200.28

Table B3. Water usage and cost.

The plant operates 12hr per day, 255 days per year. This amounts in 3060 active hours.

	Annual costs
Electricity	\$49,357.80
Catalyst	\$550.80
Water	\$4,200.28
Total	\$54,108.88

Table B4. Variable costs of production annually.**III. Fixed Costs of Production**

Our fixed costs of production come from insurance, maintenance, and labor costs. We will assume land is free of cost and property tax is negligible. We will assume we will have one laborer we pay a salary of \$43,200/year to.²⁰ We will assume maintenance is 3-5% of the ISBL annually. Insurance costs \$1,000 to \$3,000 per million, so insurance will cost \$2,100 annually.³¹

IV. Tax Calculations**Income**

Within the CV, our only source of revenue is from selling liquid CO₂. Liquid CO₂ sales prices were estimated from sale prices in 2019 as shown below:

$$\text{Cost in 2019} = \text{cost in 2014} * (\text{cost index in 2019} / \text{cost index in 2014})$$

$$\text{Cost in 2019} = \$160/\text{ton}^G * (607.5 / 556.8) = \$174.01/\text{ton}.$$

Our plant produces 147.41kg/hr, which is equivalent to 0.1625 tons/h. This yields an hourly liquid CO₂ sales of 28.27 \$/hr. We make \$86,506.20 yearly in sales.

When we include biochar sales as a source of revenue along with liquid CO₂, our income increases. Our biochar sale calculation is below:

Biochar sales = 1020 batches/year * 105 kg biochar/batch * \$2.84/kg biochar³² = \$304,164/year

Depreciation

We can claim depreciation from years 2-8. The depreciation values were calculated using the VDB (variable declining balance) function on excel, which requires inputs of the initial value, salvage value, and number of years. The excel sheet used is attached and titled Cash Flow Calculations.

Tax calculations

An excel sheet is attached that shows the amount in taxes we will pay each year for 25 years. It follows the federal tax brackets and we subtract depreciation values from our income to determine the tax bracket for years 2-8 when we can claim depreciation.

Appendix C, Environmental Considerations:

Table C1: EBC guidelines for the biochar³:

EBC - Label EBC - Class		EBC-Feed Class I	EBC-AgroBio Class II	EBC-Agro Class III	EBC-Material Class IV
Elemental analysis	C-total, C _{org} , H, N, O, S, ash				
	H/Corg	< 0,7	< 0,7	< 0,7	< 0,7
	O/Corg	< 0,4	< 0,4	< 0,4	< 0,4
Physical parameters	Water content, dry matter (DM), bulk density (TS), specific surface area (BET), pH, salt content				
TGA	Only once for the first production batch of a pyrolysis unit				
Nutrients	at least N, P, K, Mg, Ca				
Heavy metals	Pb	10 g t ⁻¹ (88%DM)	45 g t ⁻¹ DM	150 g t ⁻¹ DM	250 g t ⁻¹ DM
	Cd	1 g t ⁻¹ (88% DM)	0.7 g t ⁻¹ DM	1,5 g t ⁻¹ DM	5 g t ⁻¹ DM
	Cu	100 g t ⁻¹ DM	70 g t ⁻¹ DM	100 g t ⁻¹ DM	250 g t ⁻¹ DM
	Ni	30 g t ⁻¹ DM	25 g t ⁻¹ DM	50 g t ⁻¹ DM	250 g t ⁻¹ DM
	Hg	0.1 g t ⁻¹ (88% DM)	0.4 g t ⁻¹ DM	1 g t ⁻¹ DM	1 g t ⁻¹ DM
	Zn	400 g t ⁻¹ DM	200 g t ⁻¹ DM	400 g t ⁻¹ DM	750 g t ⁻¹ DM
	Cr	80 g t ⁻¹ DM	70 g t ⁻¹ DM	90 g t ⁻¹ DM	250 g t ⁻¹ DM
	As	2 g t ⁻¹ (88% DM)	13 g t ⁻¹ DM	13 g t ⁻¹ DM	15 g t ⁻¹ DM
Organic contaminants	16 EPA PAH	4±2 g t ⁻¹ DM	4±2 g t ⁻¹ DM	6.0+2.2 g t ⁻¹ DM	30g t ⁻¹ DM
	Benzo[a] pyren	25 mg t ⁻¹ (88% DM)			
	PCB, PCDD/F	see chp. 9	Once per pyrolysis unit for the first production batch		

Table C2: Emission guidelines followed by Carbo Culture passed by the Clean Air Act³³:

Pollutant [links to historical tables of NAAQS reviews]		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3 month average	0.15 µg/m ³ ⁽¹⁾	Not to be exceeded
Nitrogen Dioxide (NO₂)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb ⁽²⁾	Annual Mean
Ozone (O₃)		primary and secondary	8 hours	0.070 ppm ⁽³⁾	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	PM _{2.5}	primary	1 year	12.0 µg/m ³	annual mean, averaged over 3 years
		secondary	1 year	15.0 µg/m ³	annual mean, averaged over 3 years
	PM ₁₀	primary and secondary	24 hours	35 µg/m ³	98th percentile, averaged over 3 years
		primary and secondary	24 hours	150 µg/m ³	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO₂)		primary	1 hour	75 ppb ⁽⁴⁾	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

Table C3, CO₂ output from our process (Aspen):

Product stream name	Total flow (kg/hr)	CO2 flow (kg/hr)
Product (liquid CO2)	147.41	147.23
N4 (N2-rich exhaust gas)	1025.2	129.558
G2 (exhaust)	12.1	7.11
W3 (waste water)	67.2	trace
W2 (ORC water)	9007.64	0
W5 (waste water)	360.306	0

References:

1. <https://www.un.org/sustainabledevelopment/climate-change/>
2. Masson-Delmotte, V., Zhai, P., Pörtner, H. -O., Roberts, D., Skea et al. IPCC. (2018). *Global Warming of 1.5 °C. An IPCC Special Report on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty.*
3. EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland. (<http://European-biochar.org>). Version 9.1E of 25th September 2020.
4. [https://www.globenewswire.com/news-release/2020/07/08/2059486/0/en/The-Global-Biochar-Market-is-expected-to-grow-from-USD-1-385-94-Million-in-2019-to-USD-3-457-61-Million-by-the-end-of-2025-at-a-Compound-Annual-Growth-Rate-CAGR-of-16-45.html#:~:text=Filings%20Media%20Partners-,The%20Global%20Biochar%20Market%20is%20expected%20to%20grow%20from%20USD,Rate%20\(CAGR\)%20of%2016.45%25](https://www.globenewswire.com/news-release/2020/07/08/2059486/0/en/The-Global-Biochar-Market-is-expected-to-grow-from-USD-1-385-94-Million-in-2019-to-USD-3-457-61-Million-by-the-end-of-2025-at-a-Compound-Annual-Growth-Rate-CAGR-of-16-45.html#:~:text=Filings%20Media%20Partners-,The%20Global%20Biochar%20Market%20is%20expected%20to%20grow%20from%20USD,Rate%20(CAGR)%20of%2016.45%25)
5. Umeki, K., Son, Y.I., & Namioka, T. Kowalik, P. Basic Study on Hydrogen-Rich Gas Production by High Temperature Steam Gasification of Solid Wastes. *Journal of Environment and Engineering*, 2009, 4(1), 211-221. Doi: 10.1299/jee.4.211
6. Novel Renewable Double-Energy System for Activated Biochar Production and Thermoelectric Generation from Waste Heat. Wei-Hsin Chen, Kuan-Ting Lee, Yi-Kai Chih, Chun-Fong Eng, Hong-Ping Lin, Yi-Bin Chiou, Ching-Lin Cheng, Yi-Xian Lin, and Jo-Shu Chang. *Energy & Fuels*, 2020, 34 (3), 3383-3393. DOI: 10.1021/acs.energyfuels.9b04495.
7. Hussam Jouhara, Navid Khordehgah, Sulaiman Almahmoud, Bertrand Delpech, Amisha Chauhan, Savvas A. Tassou, Waste heat recovery technologies and applications, *Thermal Science and Engineering Progress*, Volume 6, 2018, Pages 268-289, ISSN 2451-9049, <https://doi.org/10.1016/j.tsep.2018.04.017>.
8. Mamun, M.A., & Biswas, S. Waste Heat Recovery System using an Organic Rankine Cycle (ORC). *International Journal of Scientific Engineering & Research*, 3(10), Oct 2012, ISSN 2229-5518.
9. Pröll, T., Zerobin, F. Biomass-based negative emission technology options with combined heat and power generation. *Mitig Adapt Strateg Glob Change* 24, 1307–1324 (2019). <https://doi.org/10.1007/s11027-019-9841-4>.
10. Dennis Y.C. Leung, Giorgio Caramanna, M. Mercedes Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, *Renewable and Sustainable Energy Reviews*, Volume 39, 2014, Pages 426-443, ISSN 1364-0321, <https://doi.org/10.1016/j.rser.2014.07.093>.
11. Rubin, E.S., et al., The cost of CO₂ capture and storage, *Int. J. Greenhouse Gas Control* (2015), <https://doi.org/10.1016/j.ijggc.2015.05.018>.
12. Yu, Z., Miller, F., & Pfotenhauer, J.M. (2017). Numerical modelling and analytical modelling of cryogenic carbon capture in a de-sublimating heat exchanger. *IOP*

- Conference Series: Materials Science & Engineering*, 278, 1-8.
doi:10.1088/1757-899X/278/1/012032.
13. Strots VO, Bunimovich GA, Roach CR, Yu.Sh. Matros. Regenerative catalytic oxidizer technology for VOC control. *Reaction Engineering for Pollution Prevention*. 2000:113-126.
<https://www-sciencedirect-com.stanford.idm.oclc.org/science/article/pii/B9780444502155500822>. Accessed Oct 13, 2020. doi: 10.1016/B978-044450215-5/50082-2.
 14. US EPA. (2020, September 08). Overview of Greenhouse Gases. Retrieved November 16, 2020, from <https://www.epa.gov/ghgemissions/overview-greenhouse-gases>
 15. Wade, Samuel R. *Ignition Behavior and Air Quality Requirements Observed During the Carbonization of Pressurized Packed Beds of Biomass*. [master's thesis]. Honolulu, Hawaii: University of Hawaii; 2005.
 16. Grahn, D. 1994, *Energy Efficient Afterburners*, Patent 5460511.
 17. Wankat, P. Separation Process Engineering, 2nd Edition. Prentice Hall, 2007. Chapter 2.
 18. NAAQS Table. 20 December 2016. EPA.gov.
 19. Puro.earth CO₂ Removal Marketplace General Rules. June 2020.
https://static.puro.earth/live/uploads/tinymce/Puro_Documents/Puro-Rules-CO2-removal-marketplace_v2.0_final.pdf
 20. Steele et al. Life-Cycle Assessment of Pyrolysis Bio-Oil Production. (2012). *Forest Prod. J.*, 62(4): 326-334.
 21. Robert M. Campbell, Nathaniel M. Anderson, Daren E. Daugaard, Helen T. Naughton, Financial viability of biofuel and biochar production from forest biomass in the face of market price volatility and uncertainty, *Applied Energy*, Volume 230, 2018, Pages 330-343, ISSN 0306-2619, <https://doi.org/10.1016/j.apenergy.2018.08.085>.
 22. VBD Function. Corporate Finance Institute. 2020.
[https://corporatefinanceinstitute.com/resources/excel/functions/vdb-function-declining-balance/#:~:text=VDB%20is%20a%20short%20form,useful%20life%20\(%23%20of%20years\)](https://corporatefinanceinstitute.com/resources/excel/functions/vdb-function-declining-balance/#:~:text=VDB%20is%20a%20short%20form,useful%20life%20(%23%20of%20years))
 23. Depreciation. eLaws. 2020. <http://flrules.elaws.us/fac/25-30.140>
 24. Depersio, Greg. Taxes in California for Small Businesses: The Basics. 12 Dec 2019. Investopedia.com.
<https://www.investopedia.com/articles/personal-finance/102115/taxes-california-small-business-basics.asp>
 25. Orem, Tina. 2020-2021 Federal Income Tax Brackets and Federal Income Rates. 16 Nov 2020. Nerdwallet.com.
<https://www.nerdwallet.com/article/taxes/federal-income-tax-brackets>
 26. Internal Revenue Code Tax Fact Sheet. U.S. Department of Energy. Office of Fuel Energy. October 2019.
<https://www.energy.gov/sites/prod/files/2019/10/f67/Internal%20Revenue%20Code%20Tax%20Fact%20Sheet.pdf>.

27. Sands, Reed W. Federal Income Tax Treatment of Certain Transferable State Tax Credits. *The Tax Adviser*. 1 July 2012.
<https://www.thetaxadviser.com/issues/2012/jul/clinic-story-10.html>
28. Carbo Culture. (2020). *Carbo Culture Carbon Footprint Assessment*. ISO 14067. UseLess.
29. Vankeirsbilck, I. & Vanslambrouck, Bruno & Gusev, Sergei & De Paepe, Michel. (2011). Organic Rankine cycle as efficient alternative to steam cycle for small scale power generation. 8th international conference on heat transfer, fluid mechanics and thermodynamics, proceedings. 785-792.
30. “Condar Company CC-001 6 Inch Round X 2 Inch Catalytic Combustor 25 Cells/Sq Inch.” Walmart.com,
www.walmart.com/ip/Condar-Company-CC-001-6-Inch-Round-X-2-Inch-Catalytic-Combustor-25-Cells-sq-Inch/119315243.
31. “Catalytic Combustor CC-001.” Rocky Mountain Stove & Fireplace,
www.rockymountainstove.com/catalytic-combustor-cc-001/.
32. Commercial Property Insurance Cost. howmuch.net.
33. Austin, Anna. Beyond the Hype. *Biomass Magazine*, 2020.
34. NAAQS Table. 20 December 2016. EPA.gov.