

Molten Salt Technology to Address Tree Mortality by Bark Beetle Infestation

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Executive Summary

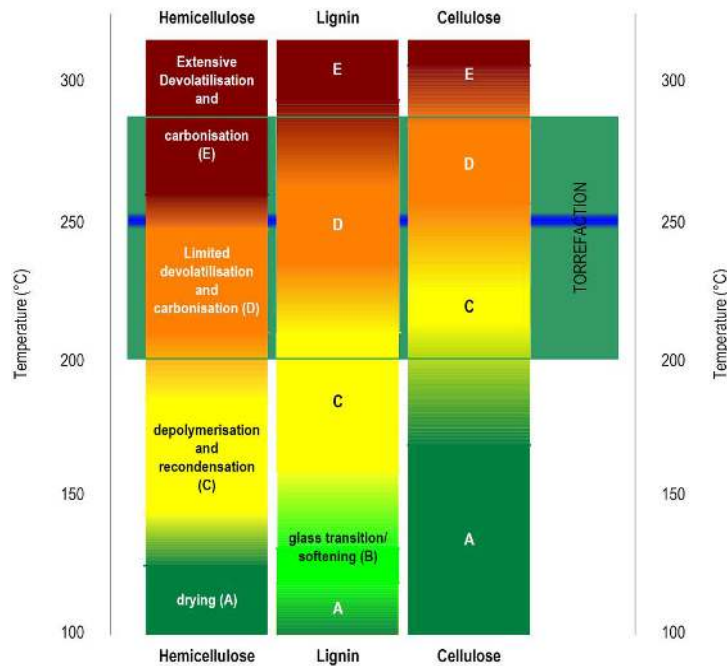
To address the problem of tree mortality by bark beetle infestation, Astron Solutions Corporation (ASC) proposes to use supertorrefaction (STR), a patented high-throughput technology which immerses wood chips contained in a porous basket under molten salt at a temperature of 450 Celsius (°C), and a slightly negative gauge pressure (pressure relative to atmospheric). The molten salt resides in a reactor vessel called the “cooker.” A cooking time of 1 minute suffices to convert the biomass into char plus flammable gases. The molten salt contains a chemical oxidant that oxidizes tars released by the biomass being heated in an otherwise oxygen-deprived environment, preventing these tars from escaping and gumming up moving parts of machinery downstream from the cooker. Charcoal fines that escape through the holes of the porous basket can also be oxidized to add heat to the surrounding salt. Net heat gains are adjusted to balance net heat losses, with the temperature of the cooker salt maintained at an average of 450 °C, batch after batch, without any input of external heat once the salt has acquired a molten state. The flammable gases are also oxidized for their heating value. Without washing, the char, covered and permeated with salt, is crushed into a fine powder that is blown in a continuous and steady manner into a second reactor vessel, called the charcoal fines gasifier and oxidizer (CFGO), with the same molten-salt composition as the cooker. The chemical oxidant rapidly oxidizes and gasifies the charcoal fines and converts this fuel with 100% efficiency to added heat of the molten salt without the release of any noxious gaseous or particulate emissions. Metal pipes carrying supercritical carbon dioxide (sCO₂) at a lower temperature but much higher pressure than the surrounding molten salt thread through the body of the charcoal fines oxidizer to create a tube-and-shell heat exchanger. The flow rate of the sCO₂ is adjusted so that the transfer of heat across the metal pipe from the hotter salt to the colder sCO₂ carries away the heat added to the salt by the oxidizing charcoal fines and keeps the molten salt of the CFGO at a constant average temperature of 450 °C. The raising of the temperature of the sCO₂ causes it to expand through the pipes a little faster so that the sCO₂ can turn a turbine that generates reliable on-demand electricity at much greater compactness of equipment than traditional gas turbines. Such sCO₂ turbines that generate 3 MWe of electricity already exist and are small enough to be held in one’s hands, but the complete system will not be built until the end of FY 2019. The combined system forms a compact unit that can be transported by truck to high hazard zones (HHZs) to convert beetle-killed pine trees as 100% of the biomass feedstock into community-scale electricity.

Background

Torrefaction entails heating biomass in an oxygen-starved environment within a typical range of temperatures 200 °C to 280 °C (Fig. 1). The traditional method burns a portion of the biomass and lets the flue gas devoid of oxygen heat the rest of the biomass in a partially enclosed environment that has a limited intake of air. The heating process drives out volatile organic compounds (VOCs), as well as water vapor.¹ The VOCs are usually burned to supplement the fuel, which can be natural gas instead of a portion of the biomass to avoid air-quality issues concerning particulate and noxious emissions.

¹ Bergman, P. C. A., Boersma, A. R., Zwart, R. W. R., Kiel, J. H. A. 2005, Torrefaction for Biomass Co-Firing in Existing Coal-Fired Power Stations, “Biocoal”, ECN-C-05-013

Figure 1. Torrefaction of woody plant material (from Bergman et al. 2005).



Low-Temperature Supertorrefaction

Supertorrefaction (STR) is an improved process invented by Frank H. Shu and developed further at Academia Sinica (patents granted in Taiwan, USA, China, Canada, and Russia) in which molten salt is used as the medium to transfer heat to the biomass with which the salt is in direct contact. In contrast with traditional torrefaction, where a few days are required for the completion of the charring process, supertorrefaction at 300 °C requires typically only ten minutes because the heat capacity of molten salt per unit volume is about 2000 times larger than that of flue gas if both heat-transfer fluids are at atmospheric pressure and a given temperature. The main advantage of STR relative to traditional technologies is that to achieve a given throughput of many metric tons (tonne) of biomass processed per day, the equipment can be much more compact. For practical operations, one can transport the equipment by truck to remote sites and thereby use beetle-killed pine trees in HHZs as 100% of the biomass feedstock to generate community-scale electricity.

Total immersion in the molten salt automatically excludes air, and if the temperature of the salt is 300 °C, a product *char* results that retains about 80% of the heating value of the original biomass. The char contains non-volatilized resins that can be detected by assaying the hydrogen content in the char relative to the fixed carbon. Volatilized resins that later condense on cold metal surfaces also appear as brown stains inside equipment that uses a mild salt that is molten at 228 °C and thermally decomposes above 400 °C. For simplicity we group all tars with the char fraction in Table 1, which also shows the VOC by-products that result from supertorrefying 20 kg of leucaena, native to Mexico and an invasive species common to much of Southeast Asia at a temperature of 300 °C. After a residence time of ten minutes under the molten salt, VOCs cease to bubble out of the molten salt.

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Table 1. STR of 20 kg of leucaena at 300 °C for 10 minutes			
Bio-product	Amount (kg)	Heating Value (MJ/kg)	Boiling point at 1 atm
Char & tar	10.724	22.99	--
Furfural C ₅ H ₄ O ₂	0.015	24.42	162 °C
Acetol C ₃ H ₆ O ₂	0.012	20.63	145 °C
Acetic Acid C ₂ H ₄ O ₂	2.475	26.41	118 °C
Water H ₂ O	4.573	0.00	100 °C
Methanol CH ₄ O	0.207	19.93	65 °C
Carbon Dioxide CO ₂	1.477	0.00	-57 °C
Methane CH ₄	0.019	55.50	-164 °C
Carbon Monoxide CO	0.496	10.11	-192 °C
Hydrogen H ₂	0.002	145.80	-253 °C
Total bio-product	20.000		--

A perusal of Table 1 shows that the list divides into two categories – the condensables (at STP): furfural, acetol (also called hydroxyacetone), acetic acid, water, methanol; and the incondensables (sometimes called “syngas”): carbon dioxide, methane, carbon monoxide, hydrogen. The acid (which corrodes the equipment) and the tar (which can gum up the moving parts of the machinery), complicate the utility of the products of traditional torrefaction and supertorrefaction, when carried out at a relatively low temperature like 300 °C. We therefore consider low-temperature supertorrefaction, as well as traditional torrefaction, unsuitable to address the problem at hand.

High-Temperature Supertorrefaction

If we change the STR salt to a more corrosive variety with a melting point of 393 °C, we can operate the cooker at a temperature between 450 °C and 600 °C (beyond which the salt will begin to thermally decompose). We then typically find that VOCs cease to bubble out of the molten salt after the biomass has been submerged under the molten salt for 1 minute or less. Table 2 gives the yields from the supertorrefaction of 20 kg of leucaena at 550 °C for 1 minute.

Table 2. STR of 20 kg leucaena at 550 °C for 1 minute			
Bio-product	Amount (kg)	Heating Value (MJ/kg)	Boiling point at 1 atm
Char & tar	6.00	26.46?*	--
Water H ₂ O	11.00	0.00	100 °C
Carbon Dioxide CO ₂	0.10	0.00	-57 °C
Methane CH ₄	0.74	55.50	-164 °C
Carbon Monoxide CO	1.48	10.11	-192 °C
Hydrogen H ₂	0.68	145.80	-253 °C
Total bio-product	20.00		--

*Not enough char produced at these conditions to have a definitive assay by Taipower.

Table 2 shows a great simplification in that, aside from water, all volatilized complex molecules, including low boiling-point tars, have been broken down by the thermochemistry of the harsher molten salt into the relatively small molecules that characterize syngas: carbon dioxide, methane, carbon monoxide, and hydrogen. The latter substances, if separated by existing membrane technology, are commercially valuable chemicals. However, being “permanent gases” at normal temperatures and pressures, they are difficult to store at remote sites (HHZs), even if we collaborated with

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experts in membrane technology who are known to us. The other choice is to oxidize the syngas for its heating value, or to combust it in a syngas engine to generate electricity for on-site and local use.

China produces a lot of syngas using coal-to-gas technology in an effort to make the combustion of coal a cleaner activity. They have developed large piston internal combustion engines that can handle syngas (with some periodic cleaning) even if the syngas is contaminated with some tar. Figure 2 shows one of the Chinese syngas engines manufactured by Ettes Power Company coupled to an alternator from the Siemens Corporation to generate AC electricity.

Although reasonably priced, even the smallest unit that only generates 300 kWe may be difficult to transport on a truck to remote HHZs. Thus, until we have a better solution for the syngas that is generated at remote sites, we will begin by oxidizing our syngas (which has no detectable amount of tar) for its heating value. To lessen the production of syngas relative to char, we also perform the STR at a lower temperature than 550 °C.

Figure 2. Syngas engine in grey with large pistons on the right coupled to a Siemens alternator in blue on the left. A red fire extinguisher at the extreme right provides scale. (<http://www.ettespower.com/Biomass-Syngas-Generator.html>)



Moderate Temperature Supertorrefaction and Oxidation

For our proposal, not only is lowering the amount of syngas production relative to char formation desirable, but so is adding a chemical oxidant to the STR salt so that we can destroy charcoal fines that escape from the porous basket that holds the wood chips. Figure 3 shows the result: a pilot scale reactor vessel containing our corrosive salt at 450 °C to which we have added a modest amount of oxidant salt. We call such a vessel a charcoal fines oxidizer (CFO).

Figure 3. Pilot scale CFO built by ASC on the campus of National Tsing Hua University (NTHU). On the left is the control panel that shows the temperature at various points on the body of the CFO, as well as the air temperature above the molten salt in the CFO. On the right is the CFO encased in green insulation with various input and output ports for experimental measurements of biomass, charcoal fines, and gaseous emissions.



Figure 4 shows what the molten salt inside looks like after dumping ½ kg of charcoal fines (CF) into the charcoal fines oxidizer (CFO). After closing the lid and turning on an internal stirrer that drags the CF into the interior of the molten salt, the CF can be seen to be chemically oxidized (at liquid densities) by the oxidizer salt in the sense that a thermocouple inserted into the salt measures a steady rise in the temperature even if the external heaters to the system are turned off. Within the accuracy of the measurement (1 °C), the salt rises in temperature by exactly the amount expected from knowing the heating value of the deposited CF and the heat capacity of the molten salt contained in the CFO, if we assume that the oxidation of the CF occurs with 100% efficiency of heat transfer to the surroundings. The energy loss through the surfaces of the pilot scale equipment with sufficient insulation is negligible on the time scale at which CF oxidation occurs.

Figure 4. Left: black opaque appearance of the molten salt after dumping ½ kg of charcoal fines into the CFO. Right: original appearance of salt after the complete oxidation of the charcoal fines has occurred.



Note that the disappearance of carbon black in the system is confirmed by salt that has been splashed by the stirrer to condense into a white solid at the top surfaces of the apparatus that are below the melting point of the mixed salt in the CFO. Also good news is the absence of any brownish stains that appear on the relatively cold top surface that would indicate the condensation of tar in the system. Evidently, any tar left in the charcoal fines is completely oxidized by the molten salt of the CFO.

To replenish the oxidant from its reacted form in the CFO, it suffices to mix in ambient air, either during the oxidation process or after it is completed. However, the sparging of cold air into the reactor vessel and the heating of the cold air bubbles as they rise slowly through the molten salt clearly yields a loss of heat for the molten salt system. Thus, the reactor vessel can be used also as a supertorrefier of biomass where the net temperature rise and fall can be controlled by how much CF gets through the holes of the porous basket and the rate at which we sparge in cold air. By empirically controlling these variables, it is possible to hold the temperature of the STR/CFO steady on average at 450 C without adding external sources of heat. We can also hold the concentration of oxidant salt at a desired level, without adding costly chemical reagents to restore its level. Successive baskets of wood chips that need supertorrefaction into charcoal pieces (what does not get through the holes of the basket) must be balanced against the leakage of charcoal fines (what leaks through the holes of the basket) that need oxidation, as controlled in part by the rate of sparging air,

Steady Heat Generation from Wood Chips By Double Cooking

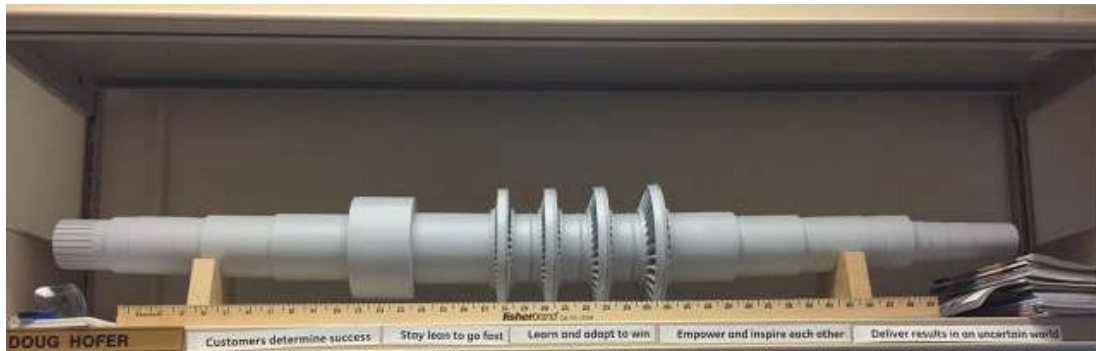
Consider building two reactor vessels that contain the same molten corrosive and oxidizer salts. Into the first reactor that we call a cooker (or STR/CFO), we lower porous

baskets of wood chips whose temperature is held at a mean equal to 450 °C without the input of an external source of heat, and whose oxidant concentration equilibrates at some desired level without adding chemical reagents other than air, in the manner we discussed before. From this cooker, we empty basket after basket of salty charcoal pieces that did not slip through the holes of the porous basket. At the pilot plant we find that we can easily grind these pieces of charcoal into a fine powder (CF). We should be able to blow this powder in a steady stream into a second reactor vessel that we call the gasifier/oxidizer (or CFGO). The CFGO gasifies and oxidizes the CF for its heating value. Because there is now a much larger amount of CF in the form of a powder than was produced in the cooker, the heating value of the CF will try to increase the temperature of the molten salt in the CFGO at a much faster rate than we can offset by a reasonable level of air sparging. Some other coolant will need to be introduced to keep the molten salt at an average temperature of 450 °C. We propose to thread the body of CFGO with pipes carrying supercritical carbon dioxide (sCO₂) that act as such a coolant. The use of such pipes makes the CFGO a device known in the trade as a tube-and-shell heat exchanger.

Electricity Generation with a sCO₂ Brayton Cycle

Figure 5 shows a sCO₂ turbine that General Electric manufactured to convert the heat of molten salt (nominally for the overnight storage of heat at a solar thermal installation) into mechanical expansion of a sCO₂ working fluid. The turbine, called the “sunrotor,” is shown inside a bookcase that contains a meter stick for scale. One could comfortably grasp this tiny turbine between two hands, yet it is theoretically capable of generating 10 MWe of electricity if 20 MWt of heat at a mean temperature of 550 °C were transferred to the sCO₂ fed into the turbine. At 450 °C, the efficiency would be somewhat reduced below 50%, but the remarkable properties of a working fluid that does not distinguish between the gaseous state and the liquid state makes possible a very great reduction of the sizes of the electricity generation equipment. (Compare the size and capacity of this turbine with those of off-shore wind turbines that stand 60 stories high or even gas turbines on jet airplanes that have much larger intake ports because their inlets are not taking in gas that has a density a hundred times that of air at sea level.)

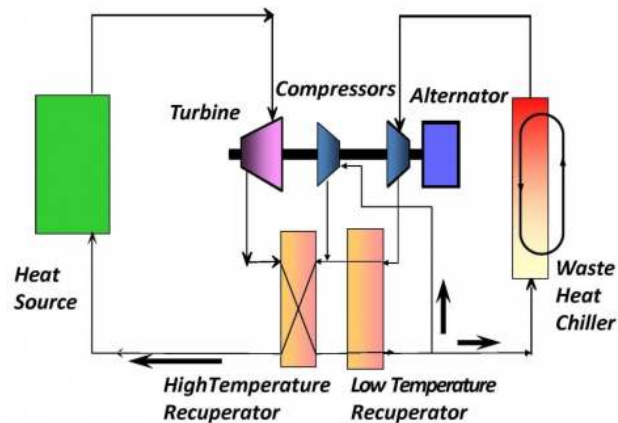
Figure 5. Sunrotor sCO₂ turbine built by General Electric that has a nominal capacity to generate 10 MWe of electricity from a 20 MWt input of molten salt at a mean temperature of 550 °C. (<http://cdn.slashgear.com/wp-content/uploads/2016/03/Screen-Shot-2016-03-09-at-2.27.24-PM.png>)



Many R&D groups are studying the peripheral equipment needed to run a Brayton cycle in which a sCO₂ turbine lies at the heart of the system (once one has a suitable source of reactor heat). Figure 6 shows a schematic diagram of a system proposed by Sandia

National Labs, which hopes by the end of FY 2019 to have a working demonstration at 550 °C operational temperature for the turbine with 10 MWe output electrical power. If we operate a system rated at 10 MWe sub-optimally (at lower temperatures and pressures of the sCO₂ gas), we can meet the community-scale limit of 3 MWe.

Figure 6. Demonstration 10 MWe Brayton cycle system proposed by Sandia National Labs with a goal to be fully operational by the end of FY 2019 at 550 °C characteristic temperature for the sCO₂. (<http://energy.sandia.gov/energy/renewable-energy/supercritical-co2/>)



Technology Readiness

STR and CFO equipment at a pilot scale exists in ASC's facility in Hsinchu, Taiwan (Fig. 7), where ASC has demonstrated the technical viability of the industrial processes by scaling up laboratory experiments by a throughput factor exceeding 100 without loss of quality of any of the biofuel products. Another scale-up by a factor of about only 4 is needed to reach the "community scale" generation of 3 MWe of electricity.

Figure 7: Equipment inside a tin shed. (Left) VOC burner. (Right) Remaining equipment: melter inside pit with immersed molten salt pump, elevated heater, cooker and condenser for bioliquids in middle, wash basins in foreground.



Relevance to the Problem of Tree Mortality

One can assess the potential of our proposal to address the problem of tree mortality in High Hazard Zones (HHZs) in the following manner. We could scale up the routine (not maximum) capacity of 10 kg of wood chips per basket by a factor of 128 and still have equipment that would be transportable on trucks to remote HHZs. Thus, having transportable equipment to generate a steady 3 MWe of electricity from beetle-killed pine trees, which needs a scale-up of only a factor of 4 from pilot scale, or a feed rate of about 28.8 tonne of wood chips per day, is not difficult. It requires only the solution of the problems of automatic loading and coupling to existing turbine systems. In principle,

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were there sufficient motivation and budget, we could build transportable equipment that could handle a throughput of about 920 tonne per day and that would generate almost 96 MWe of steady electricity. We furthermore note that our equipment does not require the chipping of heartwood or sapwood for its feedstock. If such wood has better uses elsewhere, we could operate on the stripped bark, small branches, pine cones, and even fallen pine needles if these materials could be gathered after other users have removed the heartwood and sapwood of the tree trunk.