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PNNL-35534

Integration of Autothermal Oxidation into Hydrothermal Liquefaction

January 2024

Michael R Thorson
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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Abstract

This report examines incorporating a mild oxidation process, in traditional Hydrothermal Liquefaction (HTL). The focus is on improving efficiency through heat recovery and autothermal operations. In WAO, pressurized and heated sludge, mixed with air, undergoes combustion reactions, generating CO2 and other gases. A novel aspect is using reactor effluent heat to pre-heat incoming sludge, minimizing energy needs and enabling autothermal reactions at specific solids concentrations. The report discusses many advantages of this embodiment of the HTL process, which could eliminate heat exchangers by leveraging heat from oxidation. This approach simplifies operations.

Acknowledgments

This research was supported by the Strategic Investments Initiative, under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

Acronyms and Abbreviations

WAO	Wet Air Oxidation
SCWO	Supercritical Water Oxidation
HTL	Hydrothermal Liquefaction

1.0 Integration of Autothermal Oxidation into H:

Adding oxygen or air to sludge under elevated temperatures and pressures is known to oxidize the contained organic material. The most common application of this process is known as Wet Air Oxidation, or WAO. Sludge is pressurized and heated, most economically heated by the hot reactor effluent in a heat exchanger, then mixed with pressurized air and a combustion reaction spontaneously occurs. The combustion reactions produce CO_2 and other gases, which are separated in a downstream Gas-Liquid separator. The liquid product is then further heat exchanged to warm the incoming sludge feed. Solids are then separated before the liquid effluent is released downstream.

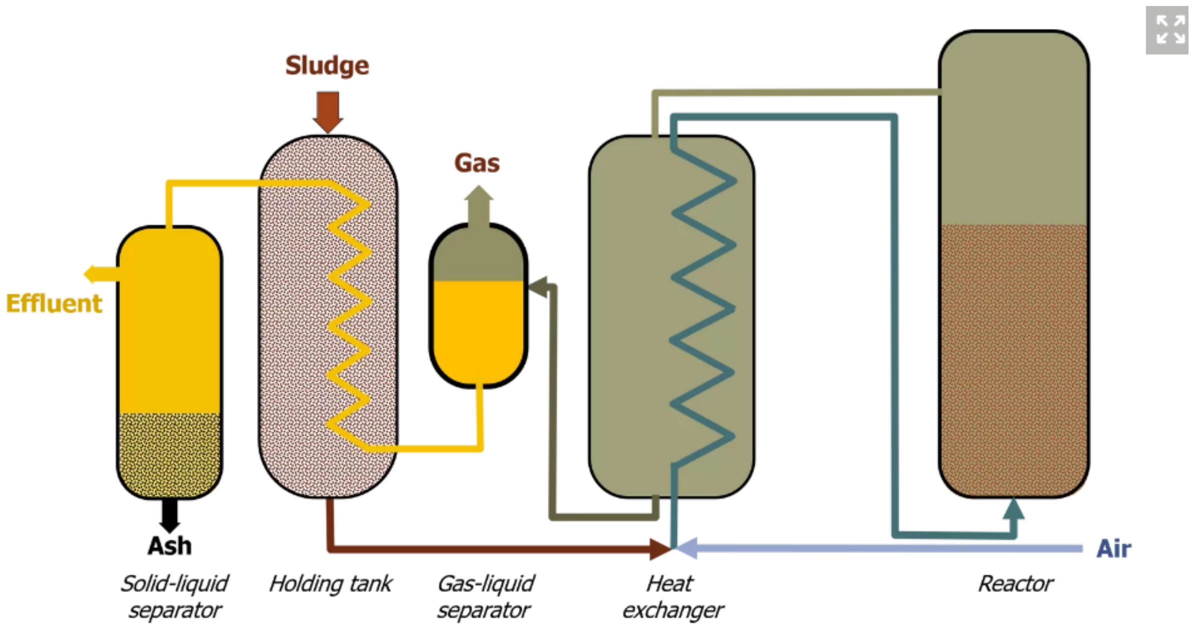

Figure 1 – Simplified wet air oxidation process

The oxidation reactions are exothermic and the sludge stream is self-heated as it reacts. Therefore, the reaction rate accelerates as the stream progresses through the reactor due to increasing temperature. A minimum temperature is required to kickoff the oxidation process. If the reactor inlet temperature does not meet a minimum threshold, oxygen will not react to create an exotherm across the reactor. Reactor inlet temperatures are usually in the range of 100-250 °C. These minimum temperatures can be achieved by the heat recovery process described in PNNL's invention (www.pnnl.gov/publications/pnnl-announces-hydrothermal-liquefaction-innovation).

The temperature increase across the reactor provides the energy to heat the incoming feed, which can be enough to heat the feed to the necessary inlet reactor temperatures. Under these conditions, the process is known as "autothermal" as it is thermally self-sustaining. Sludge oxidation in WAO is generally considered to be autothermal when the solids concentration is above 10%wt.

A related technology is known as Supercritical Water Oxidation (SCWO) of sludge, which operates at temperatures and pressures above the critical point of water (3,200 psig, 374 °C). SCWO was originally commercialized in the 1980's, but the technology has since declined due to operational and reliability challenges. The process is corrosive due to oxygen, CO_2, and byproduct organic acids. Salts precipitate and foul surfaces or restrict fluid flow.

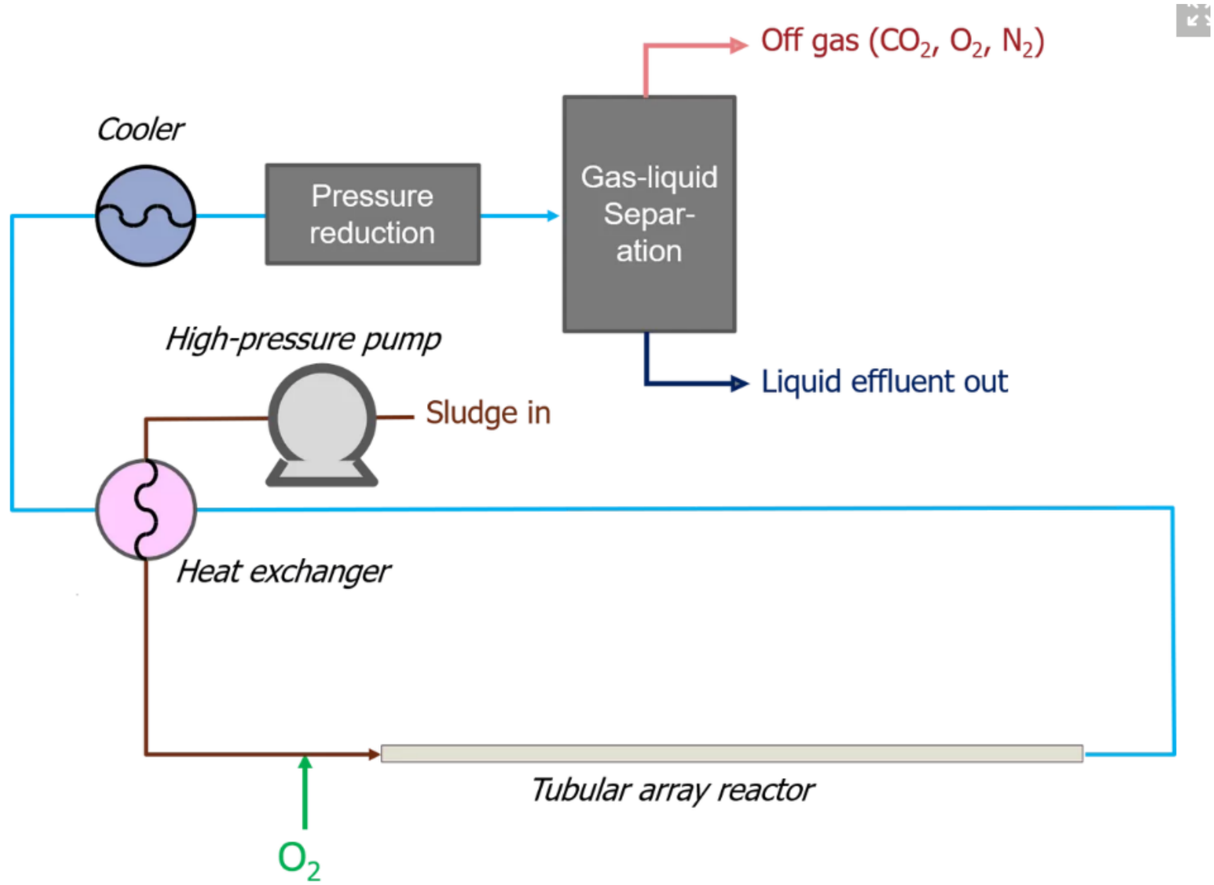

Figure 2 – Example of supercritical water oxidation process for sewage sludge treatment.

Both processes described above rely heavily on heat exchangers to recover energy from the reactor product. These heat exchangers are a major sources of their reliability issues.

The traditional Hydrothermal Liquefaction (HTL) process has a similar equipment configuration to WAO and SCWO. HTL has all the same parts (high pressure pump, feed/product HX, reactor, heat exchange, pressure letdown), minus the addition of oxygen.

According to PNNL's patented invention, all heat exchangers can potentially be avoided in the HTL process by using oxidation to increase the sludge temperature across the reactor, then transferring the heat gain to the feed with the hot gases and steam generated by letting down the pressure at the HTL reactor outlet. Similar to commercially deployed WAO or SCWO autothermal reactors, PNNL's system, illustrated in the figure below, would be simple and would not require catalysts or complicated internals, aside from what is required to ensure the oxygen is well-mixed with the sludge. The reactors could be tubular with oxygen injection at multiple points to ensure good mixing. The rate of oxygen injection would be controlled to meet the desired reactor outlet temperature. Excessive oxygen injection would consume additional sludge or biocrude product.

Traditional HTL (no oxygen addition) generates CO_2 byproduct gas, with CO_2 being up to 5%wt of the reactor effluent. Injecting oxygen for combustion will generate additional CO_2. The amount of required O_2 addition and CO_2 formation will depend on the heating value of the sludge and which components are oxidized (these details are not known at this time). The current estimate is that the reactor effluent CO_2 concentration will increase to 9-10 wt% CO_2, or roughly doubling the CO_2 production over traditional HTL.

It should be noted that the process would separate the CO_2 and recover much of the energy from the hot gases by bubbling the gas through the incoming sludge feed in D-1 and D-2. The CO_2 leaves the process with the other byproduct non-condensible gases in the D-1 overhead line routed to "Acid Gas Treating". This stream will contain a high concentration of CO_2 (estimated 82% mass or 72 %mole), making carbon capture possible to improve the carbon intensity of HTL.

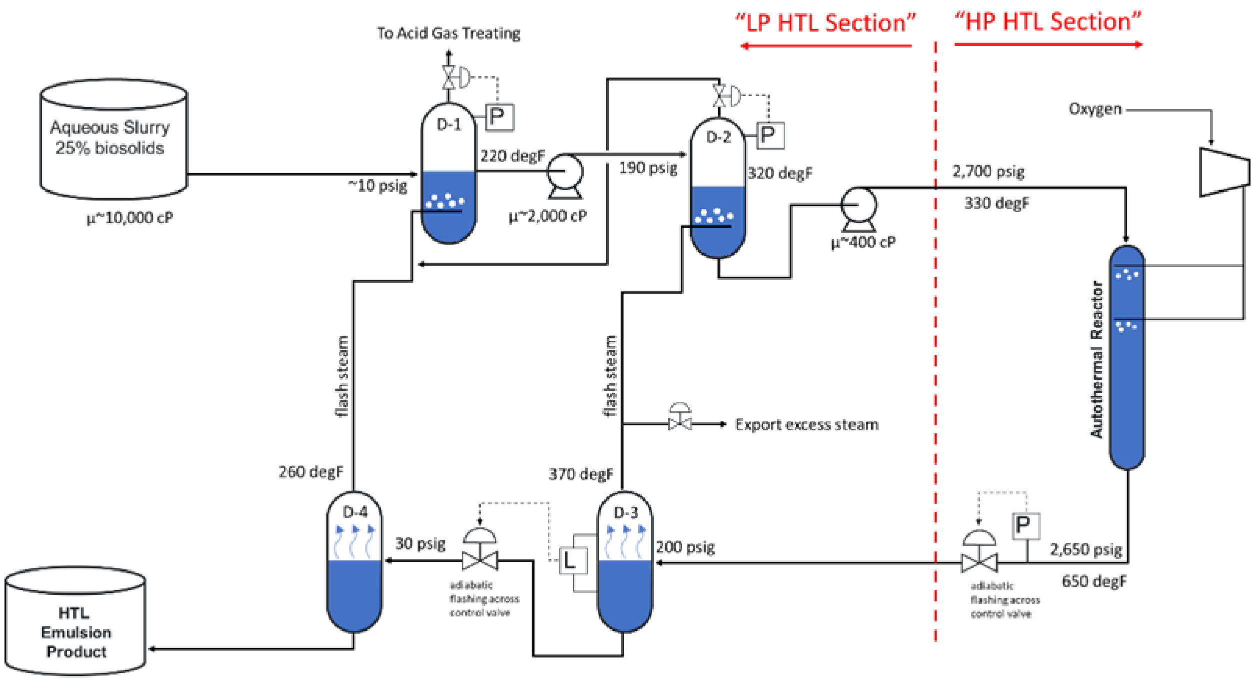

Figure 3. PNNL's innovative HTL process, including autothermal HTL

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