

# **RECOVERY OF LIQUID CO<sub>2</sub> AND PARTICULATES FROM BIOMASS-FIRED POWER PLANTS USING PRESSURIZED COMBUSTION**

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## **SUMMARY**

The novel<sup>1</sup> pressurized oxy-fuel or air-blown approach known as the ThermoEnergy Integrated Power System (TIPS) is a carbon-capture capable concept designed to produce electricity and steam from high-moisture fuels with near zero air emission of priority and toxic pollutants. The increased system pressure enables use of gas-to-liquid steam-hydroscrubbing to collect and remove pollutants and recover latent heat from water entrained or produced in the combustion process. The pressurized oxy-fuel approach also enables CO<sub>2</sub> to be recovered as a pressurized liquid through direct condensation. This paper examines models of pressurized combustion using air-blown and oxygen-enriched air-blown systems. For the air-blown process, air compressors are reliable but consume a relatively high amount of parasitic power. Pressure-swing adsorption and turbine expansion of the flue gas in these air-blown systems are being modeled and evaluated as ways to reduce or mitigate parasitic power losses. Subsequent modeling will examine the oxy-fuel approach using oxygen of varying degrees of purity from cryogenic air separation units.

Pressurized combustion technology addresses two major issues affecting the future use of the country's coal and biomass resources: (1) economic capture of criteria and toxic pollutants (such as mercury) from the diverse power and steam generators needed, and (2) economic capture of CO<sub>2</sub> from the larger power and steam generators used by utilities and large industrial facilities. TIPS requires relatively few unit operations and can use proven oxygen sensor instrumentation for process control. The fewer unit operations and excess oxygen combustion regime suggests that TIPS can be a reliable – high capacity factor - technology on which to base the nation's coal-to-steam-and-power future. The simplicity of TIPS may enable smaller economic units that could be located closer to the loads thereby reducing transmission losses.

## **INTRODUCTION**

Current modeling and development work underway includes an evaluation of the TIPS process using three alternative modes of pressurized combustion of coal and biomass. The process choices being evaluated include the use of air, oxygen-enriched air from a pressure-swing adsorption plant and oxygen from a cryogenic oxygen separation plant.

The objective for examining the three different options is to have a basis of comparison between them. The air-blown unit will require a large air compressor, but not an air separation unit. Pressure-swing adsorption is a simple proven process that essentially doubles the oxygen concentration and halves the compression equipment and power needed to pressurize the oxidant. These first two options will produce a clean carbon dioxide – nitrogen gas mixture as the product/exhaust. The interest here is to assess the potential benefit of pressurized combustion

in a regime where carbon dioxide was not initially captured but the overall system retained that capability. The conversion to carbon capture would be added on either by subsequent flue gas treatment or by conversion to oxygen-blown operation.

### **TIPS PROCESS DESCRIPTION**

TIPS process combustion takes place at pressures between 4.83 and 8.96 MPa. (700 and 1300 psia) Increasing the pressure of combustion shifts the temperature at which water, CO<sub>2</sub> mercury and acid gases condense. The elevated pressure and condensation temperature process conditions enable TIPS to utilize heat transfer, mass transfer and liquid vapor equilibrium regimes well suited to capture of pollutants and CO<sub>2</sub>. Elevating the pressure enables TIPS to use the phenomenon of nucleate condensation at temperatures in the range of 262 to 303°C (503 to 577°F) in a heat exchanger that simultaneously recovers heat and condenses and captures pollutants.

Two components of pressurized oxy-fuel technology central to achieving the twin goals of efficiency and pollution control are (1) the air separation plant to provide oxygen under pressure, and the (2) condensing heat exchanger to capture both pollutants and heat from the combustion gases.

There is potential for pressurized combustion with an air-blown system, with the same pressure range as the oxy-fuel TIPS process. Air compressors are highly reliable devices. However, initial models show that air compression consumes a high percentage of the system power to compress air to the operating pressure. This parasitic power decreases by 55 percent when using pressure-swing adsorption to increase air to 35 psi and 40 percent oxygen prior to entering the compressor.

### **Condensing Heat Exchanger Recovers Heat and Captures Pollutants**

The TIPS configuration enables the condensing heat exchanger to collect particulates, acid gases and mercury into a condensed phase that is roughly 2,500 to 3,500 times smaller than the volume of gas treated by conventional atmospheric pressure flue gas clean-up systems. The nucleate condensation phenomenon is so rapid and so efficient that, once developed, the TIPS process may be less costly than current atmospheric pressure systems requiring particulate collection, desulfurizers, de-NO<sub>x</sub> and mercury abatement equipment.

The curves in Figure 1 correspond to the pure component liquid vapor equilibrium lines for water, and carbon dioxide. The curves show the effect of increasing the pressure on condensation temperature of the main exhaust gases. The higher pressure corresponds to a higher liquid-vapor equilibrium temperature for the gaseous components of the exhaust. TIPS makes use of this pressure-induced temperature shift to enable the recovery of heat, condensation of pollutants and removal of particulates from the exhaust gases.

Position 1 shows the point at which a dirty exhaust gas would exit the radiative section of the pressurized combustion and heat transfer unit. Liquid water sprayed into this gas rapidly evaporates and cools the exhaust gas to position 2. The large surface area of the droplets in the liquid spray provides rapid heat transfer. Although the mass of the gas stream (exhaust gas plus evaporated water) is increased, the volumetric flow decreases due to the cooling of the gas. The

water spray cools the exhaust gas and rapidly moves the temperature and pressure of the combined stream to position 2 at the liquid-vapor equilibrium line for water at the system pressure. The heat energy that was in the hot exhaust gas was not lost during the cooling process. It was transformed into the latent heat of vaporization of the evaporated water. This moisture-laden exhaust stream in the current example then goes into a condensing heat exchanger at a temperature of 302°C (575°F) and a pressure of 8.8 MPa (1,276 psia). This heat exchanger transfers the heat from the moisture-laden exhaust to the boiler feed water. The boiler feed water is substantially cooler, typically ~27°C (80°F), than the temperature at which the moisture in the exhaust gas will condense. The large temperature difference between the boiler feed water and the moisture in the exhaust gas drives rapid heat transfer to condense the water in the exhaust gas and rapidly and efficiently heat the boiler feed water. The temperature of the moisture-laden exhaust gas stream, 302°C (575°F) does not change significantly as it transfers heat to the boiler feed water until the bulk of the water vapor has been condensed to liquid. This enables the heat exchanger in the current example to maintain a temperature difference suitable for efficient heat transfer. The exhaust gas is cooled below the liquid vapor equilibrium temperature to position 3. There the bulk of the moisture and energy has been removed from the exhaust gas and the remaining gas, primarily CO<sub>2</sub>, is further cooled to position 4 where carbon dioxide in the exhaust gas, if in pure form, can be condensed into a liquid. In a mixture with argon and oxygen, additional separation would be needed.

When steam or carbon dioxide is cooled and condensed into a liquid, surface forces cause the condensing gas to preferentially condense on solid or liquid surfaces. When the liquid water and carbon dioxide gas condense, the liquid material preferentially goes onto the surfaces of particles to make big droplets. Big droplets with little seed particles in them are easily removed. This phenomenon of nucleate condensation or steam hydroscrubbing exhibits very high particle capture efficiencies. Instead of avoiding acid gas condensation, this process encourages it and makes use of it to remove pollutants and recover heat. A significant benefit of using this approach is that the mass transfer driving force does not diminish as the concentration of acid gas forming materials and particulate matter decreases. The major issue relates to materials of construction and experimental data is presented in the next section.

#### SAMPLES FOR CORROSION TESTING

The condensing heat exchanger is a key component of the TIPS process and will be subjected to a severe environment of high-temperature water, oxygen and condensing acid gases. Testing of coatings and materials deemed candidates for this service was conducted as follows:

Test conditions:

- Temperatures of 250°C, 275°C, 300°C
- Test time of 72 hours
- 2-liter volume autoclave; samples located in center in a graphite holder
- Test substrate coupons 1.375- by 2.5- by 1/16 inch thick samples of TiN-coated stainless steel and of TiN-coated copper as well as Grade 7 titanium
- The coated samples had a coating thickness of about 5µm
- The Grade 7 titanium tested was uncoated

Series	250 °C	275 °C	300 °C
1 (Control)	Air at room pressure	Air at room pressure	Air at room pressure
2 (Blank)	50 psi CO <sub>2</sub>	50 psi CO <sub>2</sub>	50 psi CO <sub>2</sub>
3 (Low)	1.25 g Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> *, 0.28 g HCl, 50 psi CO <sub>2</sub>	1.25 g Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> *, 0.28 g HCl, 50 psi CO <sub>2</sub>	1.25 g Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> *, 0.28 g HCl, 50 psi CO <sub>2</sub>
4 (High)	6.5 g Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , 1.4 g HCl, 50 psi CO <sub>2</sub>	6.5 g Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , 1.4 g HCl, 50 psi CO <sub>2</sub>	6.5 g Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , 1.4 g HCl, 50 psi CO <sub>2</sub>

\*-Sodium metabisulfite used as SO<sub>2</sub> source

All tests used 150 mL of water in addition to the above reagents. This amount of water assured that wet steam conditions prevailed in all tests. Room pressure air was present in the reactor when it was pressurized to 50 psi with CO<sub>2</sub>.

The coatings all failed and the stainless steel samples were badly pitted. The Grade 7 titanium samples, the blank and test 13, are shown in the electron microscope photos shown in Figure 2. The titanium showed a blue oxide layer, no pitting and no significant corrosion. The rough surface of the Grade 7 samples is the normal appearance, both the blank and tested coupon. The Test 13 sample was tested at the high test condition, where it was subjected to a high concentration of HCl. Chemical analysis of the surface of the tested sample showed deposits of minerals and iron compounds from the dissolved and redeposited remains of previous test samples and liquid containers. The quartz and glass containers dissolved in the tests, but the Pyrex survived. The test apparatus was titanium lined and had a new thermocouple well made from Grade 4 titanium that was subjected to all 48 days of testing in all conditions. This thermowell also showed no pitting and no significant corrosion. The edges were solid and sharp and the embossed lettering edges were also still sharply defined. The test results on the samples, along with the observations made on the thermowell used in the testing apparatus, provide a preliminary indication that a number of grades of titanium may be suitable for construction of the condensing heat exchanger used in the TIPS process.

### **PROCESS MODELING**

ThermoEnergy staff are currently performing process modeling studies to compare using TIPS in the oxy-fuel mode and the air-blown arrangement. The modeling studies are focused on lignite and wood waste because of the large amount of water in these fuels. The high moisture content of wood waste (>50%) is problematic to conventional combustion but well suited to TIPS because of the ability to capture the latent heat of vaporization of water. For the model an average of the wood waste composition using data from the U.S. Forestry Service<sup>ii</sup> and the Phyllis database was used.<sup>iii</sup>

Studies are also underway to determine an efficient method of using petroleum coke with the TIPS concept of pressurized combustion. Petroleum coke has lower moisture content than wood waste (10.9%) but there is still a substantial amount of latent heat captured by TIPS. Table 1 shows the ultimate analyses used for both wood waste and petroleum coke used in the Aspen model. It also shows the ultimate analyses for the fuels that will be used in the upcoming models.<sup>iv</sup> The TIPS method for petroleum coke looks very beneficial with reliable equipment and the initial models are showing a relatively high efficiency (~33% based on the higher heating value of petroleum coke and propane). Due to the higher amount of sulfur in petroleum coke

than wood waste, some modifications were made to the model to include calculations for the conversion of sulfur dioxide to sulfuric acid. This took two equilibrium reactors<sup>v</sup> to perform the conversion ( $\text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{SO}_3$ ,  $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ ). Figures 2 and 3 show the combustion/flue gas models used in the wood waste and petroleum coke cases, respectively. Both of these cases used the pressure-swing adsorption. Figure 4 shows the Rankine Cycle used in both cases.

**Table 1 Analysis of Fuels Used in the TIPS Model**

<b>Wood Waste</b>		<b>Petroleum Coke</b>	
<i>Component</i>	<i>Mass Fraction</i>	<i>Component</i>	<i>Mass Fraction</i>
H <sub>2</sub> O	0.537	H <sub>2</sub> O	0.106
Carbon	0.510	Carbon	0.892
Oxygen	0.400	Oxygen	0.00
Nitrogen	0.00648	Nitrogen	0.0180
Hydrogen	0.0603	Hydrogen	0.0370
Sulfur	0.00389	Sulfur	0.0500
Ash	0.0194	Ash	0.00302
HHV, Btu/lb	8603	HHV, Btu/lb	13496
Volatile Matter	49.5	Volatile Matter	10.0
Fixed Carbon	49.6	Fixed Carbon	89.73
<b>Lignite</b>		<b>Illinois #6 High-Volatile Bituminous</b>	
<i>Component</i>	<i>Mass Fraction</i>	<i>Component</i>	<i>Mass Fraction</i>
H <sub>2</sub> O	0.3224	H <sub>2</sub> O	0.0797
Carbon	0.6585	Carbon	0.6565
Oxygen	0.1818	Oxygen	0.0860
Nitrogen	0.0103	Nitrogen	0.0116
Hydrogen	0.0435	Hydrogen	0.0423
Sulfur	0.0080	Sulfur	0.0484
Ash	0.0973	Ash	0.1548
HHV, Btu/lb	11001	HHV, Btu/lb	11951
Volatile Matter	44.94	Volatile Matter	36.86
Fixed Carbon	44.54	Fixed Carbon	36.47

Table 2 shows a comparison of the air-blown system with and without pressure-swing adsorption along with oxy-fuel. In all model cases, the air/oxygen/enriched oxygen stream was compressed to 800 psi with a maximum temperature setting of 350F in the air compressor stages. This table gives an idea of the total work it takes to achieve the mass flow rate of 800 psi oxygen needed to supply the combustor with 20 percent excess oxygen.

**Table 2 PSA vs. Non-PSA Compression vs. Air Separation Unit (800 psi outlet, 25000 lb/hr O2 generated)**

Non-PSA Air Compression		PSA Air Compression		Air Separation Unit (95% O2)	
Stage 1 Work	2.24 MW	Separation Work	0.28 MW	Separation Work	2.54 MW <sup>vi</sup>
Stage 2 Work	1.93 MW	Stage 1 Work	1.10 MW	Stage 1 Work	0.473
Stage 3 Work	1.54 MW	Stage 2 Work	0.95 MW	Stage 2 Work	0.437
Stage 4 Work	1.20 MW	Stage 3 Work	0.75 MW	Stage 3 Work	0.434
Total Work	6.91 MW	Total Work	3.08 MW	Total Work	1.34
Total O2 Mass	25,000 lb/hr	Total O2 Mass	25,000 lb/hr	Total O2 Mass	25,000 lb/hr
Total Gas Mass	108,700 lb/hr	Total Gas Mass	57,918 lb/hr	Total Gas Mass	26,316 lb/hr

Table 3 is a display of the inputs and outputs of the TIPS models used thus far.

**Table 3 Inputs and Outputs of 3 Aspen Models**

Inputs		Outputs	
<b><i>Case 1 – 15.0 MW<sub>e</sub> Net Wood Waste Enriched Air-Blown Plant (800 psi Operating Pressure)</i></b>			
Primary Fuel	Wood Waste	Gross Power	17.9 MW
Mass Flow	30,739 lb/hr	Gas Turbine Power	5.5 MW
HHV	8,603 Btu/lb	Steam Turbine Power	12.4 MW
Secondary Fuel	Liquid Propane	Net Power	15.0 MW
Mass Flow	700 lb/hr	8 Pound steam	4,100 lb/hr
HHV	20,000 Btu/lb	<i>Emissions</i>	
Energy In	2.78 * 10 <sup>8</sup> Btu/hr	SO <sub>2</sub>	7.23 * 10 <sup>-6</sup> lb/MMBtu
Energy In	81.7 MW	NO <sub>2</sub>	0 lb/MMBtu
Enriched Air (40% O <sub>2</sub> )	59,285 lb/hr	Hg	0 lb/MMBtu
Separation Work	0.28 MW		
Compression Work	2.86 MW		
HHV Net Efficiency	18.4 %		
<b><i>Case 2 – 11.0 MW<sub>e</sub> Net Wood Waste Oxy-Fuel (95% O<sub>2</sub>) Plant (800 psi Operating Pressure)</i></b>			
Fuel	Wood Waste	Gross Power, Steam Turbine	15.8 MW
Mass Flow	37,750 lb/hr	Net Power	11.0 MW
Recycled Flue Gas	85,000 lb/hr	8 Pound Steam	6,640 lb/hr
HHV	8,603 Btu/lb	<i>Emissions</i>	
Energy In	3.25 * 10 <sup>8</sup> Btu/hr	SO <sub>2</sub>	6.90 * 10 <sup>-6</sup> lb/MMBtu
Energy In	95.3 MW	NO <sub>2</sub>	0 lb/MMBtu
ASU Exit (95% O <sub>2</sub> )	32,921 lb/hr	Hg	0 lb/MMBtu
Separation Work	3.19 MW		
Compression Work	1.58 MW		
HHV Net Efficiency	11.5 %		
<b><i>Case 3- 15.2 MW<sub>e</sub> Net Petroleum Coke Enriched Air-Blown Plant (800 psi Operating Pressure)</i></b>			
Primary Fuel	Petroleum Coke	Gross Power	21.8 MW
Mass Flow	17,000 lb/hr	Gas Turbine Power	7.7 MW
HHV	13,496 Btu/lb	Steam Turbine Power	14.1 MW
Secondary Fuel	Liquid Propane	Net Power	15.2 MW
Mass Flow	1,300 lb/hr	<i>Emissions</i>	
HHV	20,000 Btu/lb	SO <sub>2</sub>	4.86 * 10 <sup>-5</sup> lb/MMBtu
Energy In	2.55 * 10 <sup>8</sup> Btu/hr	NO <sub>2</sub>	0 lb/MMBtu
Energy In	74.9 MW	Hg	0 lb/MMBtu
Enriched Air (40% O <sub>2</sub> )	119,564 lb/hr		
Separation Work	0.84 MW		
Compression Work	5.8 MW		
HHV Net Efficiency	20.3 %		

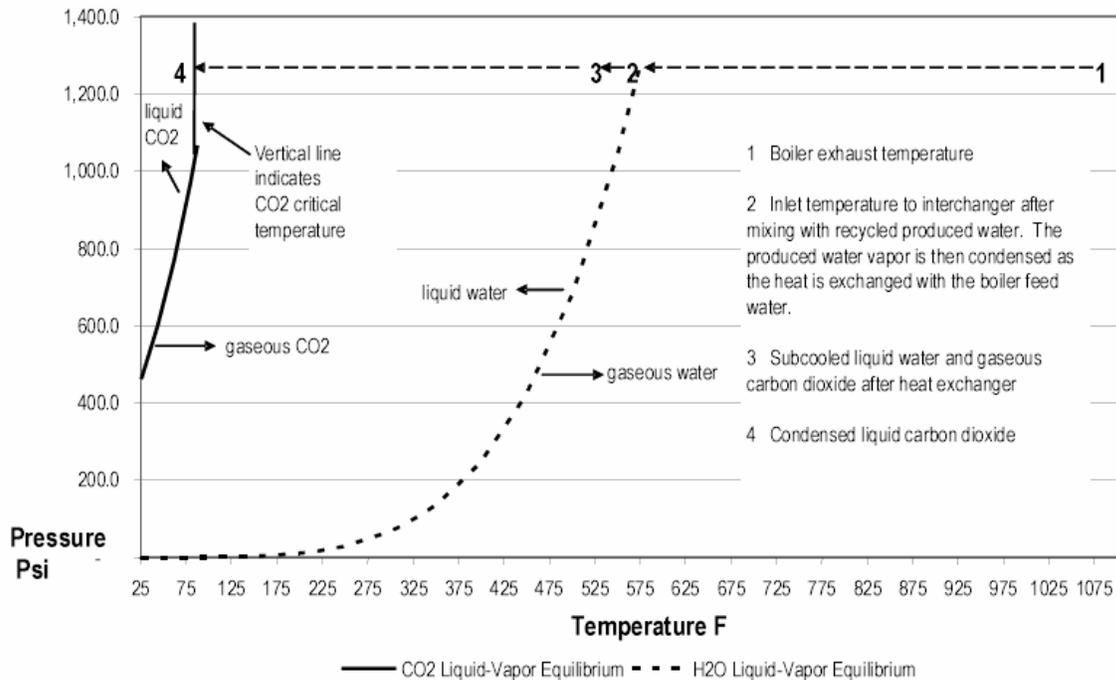
## CONCLUSIONS:

While detailed studies are still underway for the performance of TIPS pressurized combustion technology under a range of applications, preliminary estimates presented here indicate that in a carbon capture scenario:

- TIPS simplicity enhances process reliability and lessens dependence on scale,
- Implementation of advanced air separation technologies, while improving both IGCC and oxy-fuel technologies, have a greater positive effect on the oxy-fuel approach.
- Pressurized combustion using oxygen-enhanced air has a significantly lower parasitic load than the air-blown unit.
- Suitable materials are available for the construction of a condensing heat exchanger that can be expected to have an economically useful life.
- The capture of the latent heat of vaporization in the produced and entrained water is especially important in maximizing efficiency of biomass and lignite-fired systems.

Future utilization of high-moisture biomass and coal resources for heat and power will require a technology capable of capturing CO<sub>2</sub> as well the priority and toxic pollutants associated with biomass and coal utilization. The TIPS pressurized combustion/oxy-fuel technology described here can meet these requirements and merits development and deployment.

Figure 1 Pure Component Liquid Vapor Equilibrium



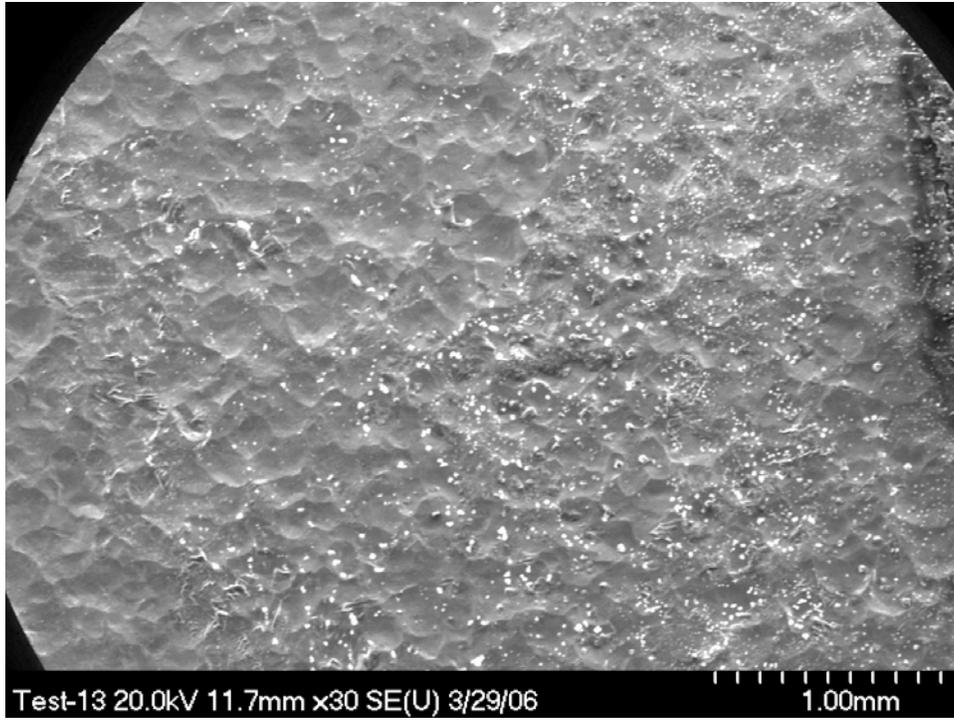
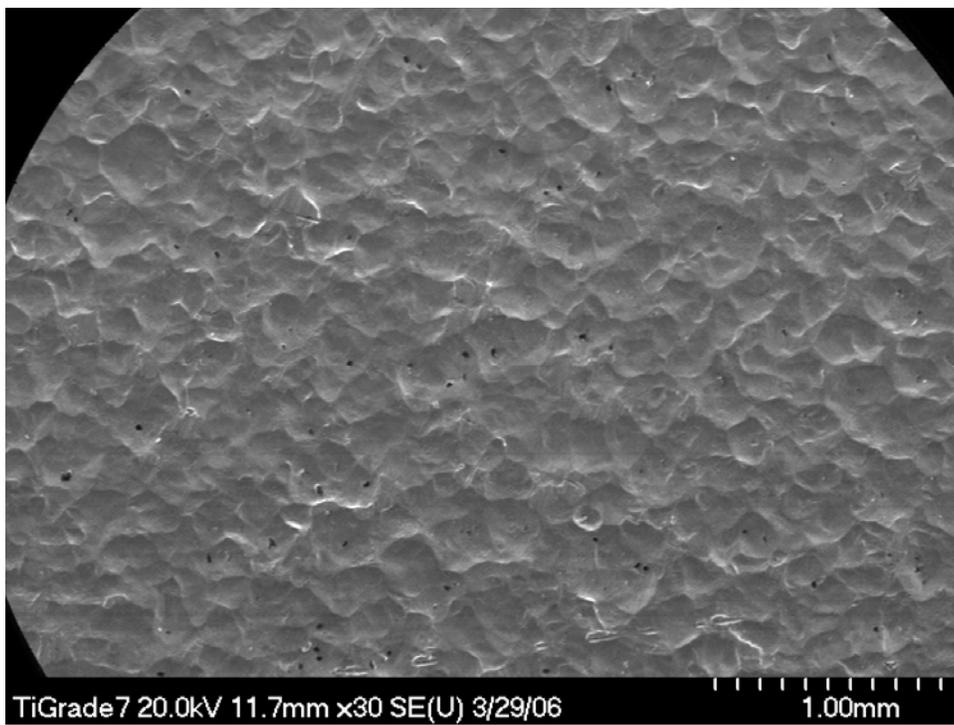


Figure 2 Photomicrograph of Titanium Grade 7





**Figure 4 Aspen Model Used For Petroleum Coke 15 MW Plant**

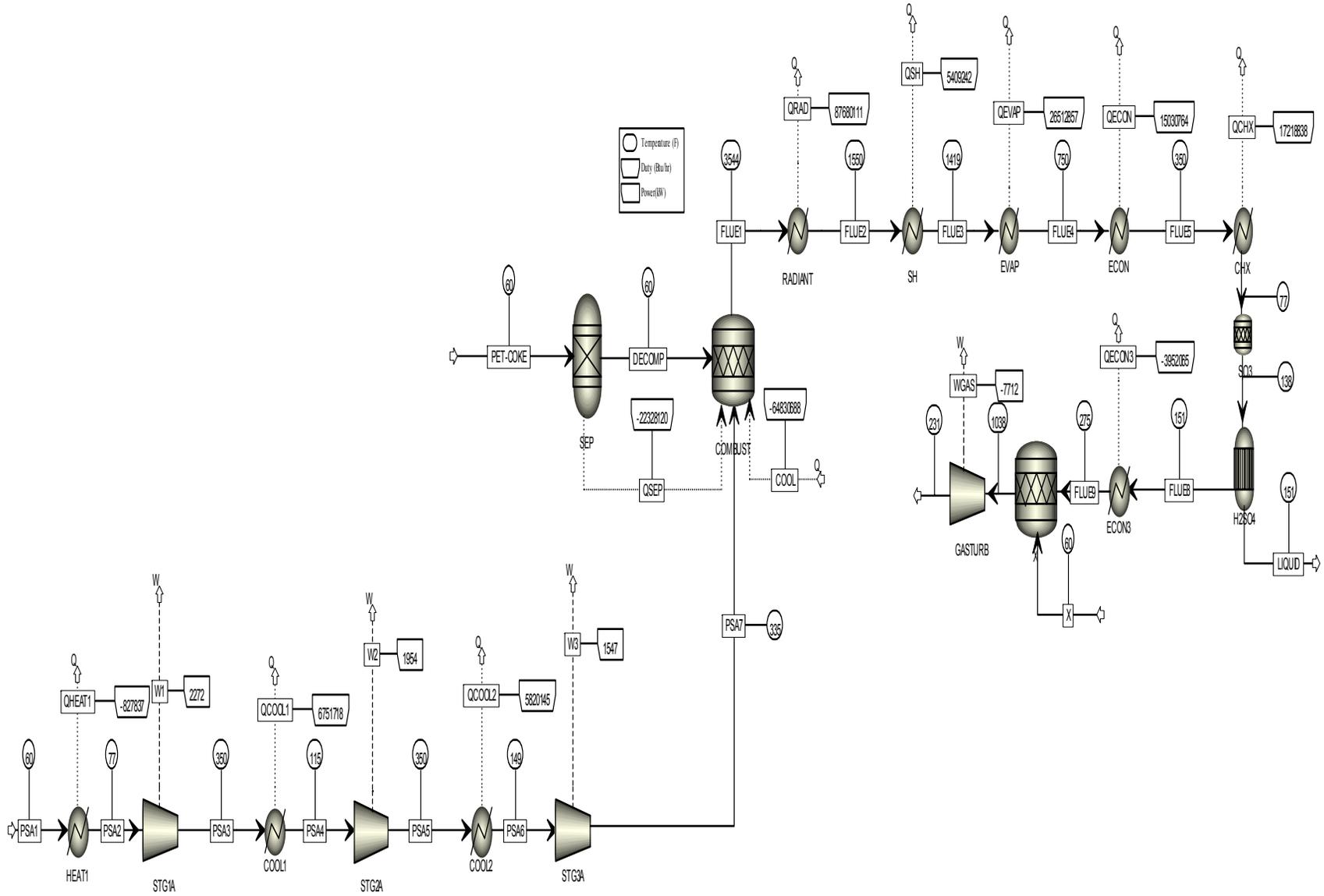
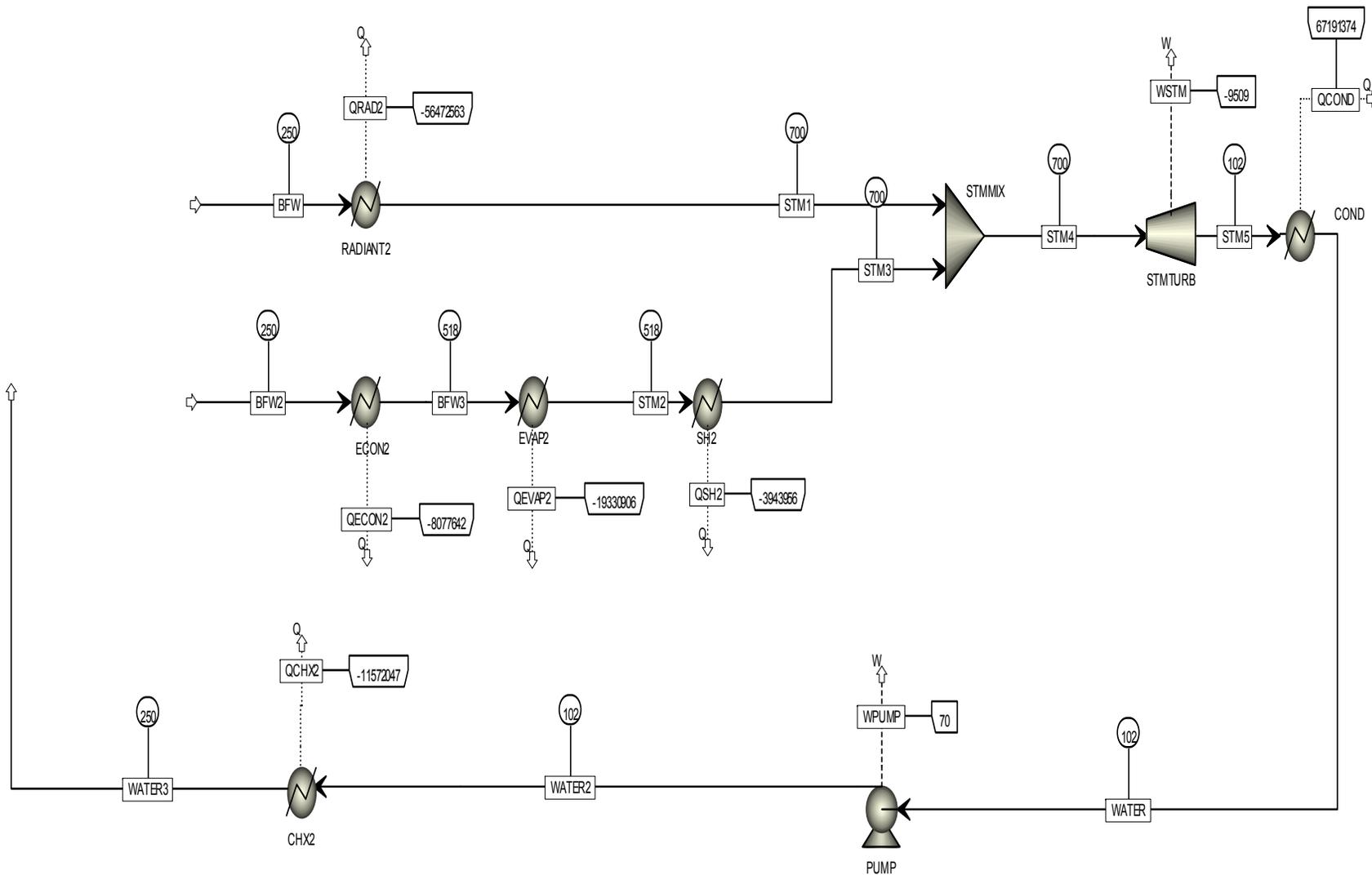


Figure 5 Aspen Model of Rankine Cycle



## References:

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- <sup>i</sup> Patent No. 6,196,000 '*Power System with Enhanced Thermodynamic Efficiency and Pollution Control*'. A.G. Fassbender.
- <sup>ii</sup> 'USDA Forest Service, Pacific Southwest Research Station'
- <sup>iii</sup> 'ECN Laboratories – Phyllis Database'
- <sup>iv</sup> 'Quality Guidelines for Energy System Studies', Office of Systems and Policy Support. NETL, Gilbert V. McGurl, Robert E. James, Edward L Parsons, John A. Reuther, John G. Wimer.
- <sup>v</sup> Aspen Plus 2004 (ELEC-NRTL Method, 2 Equilibrium Reactors in series were used to perform the  $\text{SO}_2 \rightarrow \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$  conversion)
- <sup>vi</sup> 'Advanced Fossil Power Systems Comparison Study', Edward L. Parsons, National Energy Technology Laboratory, Walter W. Shelton, Jennifer L. Lyons, EG&G Technical Services, Inc.