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COAL POWER PLANTS WITH ENHANCED PROFITABILITY AND NO CARBON DIOXIDE EMISSIONS

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Coal Power Plants with Enhanced Profitability  
and No Carbon Dioxide Emissions

A thesis submitted in partial satisfaction  
of the requirements for the degree Master of Science  
in Chemical Engineering

by

Chuanjun Jiao

2017

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2017

## ABSTRACT OF THE THESIS

### Coal Power Plants with Enhanced Profitability and No Carbon Dioxide Emissions

by

Chuanjun Jiao

Master of Science in Chemical Engineering

University of California, Los Angeles, 2017

Vasilios Manousiouthakis, Chair

A zero carbon dioxide emission process is developed, in which electrical power and formic acid are coproduced from coal. The overall reaction for the proposed process uses coal, oxygen, and water as reactants. A reaction cluster is proposed which consists of feasible chemical reactions. These are: gasification of coal to syngas; CO<sub>2</sub> hydrogenation to formic acid; hydrogen combustion; and CO combustion. By adjusting the oxygen delivery ratio, the coal gasification is designed to be energetically self-sufficient, so that the whole process produces the largest amount of power. Temperature and heat load information for each process stream is obtained from the software simulation and used in carrying out a heat and power integration study. Through the use of heat engine and heat pump subnetworks, a feasible operating envelope for the considered process is identified. A preliminary technoeconomic analysis is carried out, which establishes the superiority of the proposed process to current coal power plant technology.

The thesis of Chuanjun Jiao is approved.

Vijay K. Dhir

Yunfeng Lu

Vasilios Manousiouthakis, Committee Chair

University of California, Los Angeles

2017

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# 1. Introduction

A rapid increase in the concentration of CO<sub>2</sub> and other greenhouse gases (GHGs) in the atmosphere has created a major environment concern at the national and global level, initiating numerous efforts to mitigate its effect. In line with new environmental policies limiting annual CO<sub>2</sub> emissions, the use of cleaner fuels (e.g. natural gas) and alternative renewable energy resources has become a point of interest [1]. However, these alternatives have their own drawbacks. For example, natural gas, although a clean burning fuel, still emits GHGs [2,3]. Solar energy, another clean energy alternative, is based on regionally varied solar radiation intensity. As a result, this energy resource might be scarce in those areas where solar radiation is insufficient. Wind energy is less applicable in developing countries because the incompleteness of data systems in those countries leads to difficult decisions regarding investment in wind electricity, which eventually makes wind power less sustained [4].

Fossil fuel (coal, natural gas, crude oil) combustion and utilization is notorious for increasing the amount of GHGs in the atmosphere [5], and among these, coal is most infamous because it generates large amounts of carbon dioxide per unit electricity produced through combustion. It is the most plentiful fuel in the fossil fuel family and its first use can be traced back to about 1900 years ago. Through centuries of exploration, technology related to coal mining and other treatments, such as gasification or liquefaction, has been well honed and completely developed. Its many uses include heating, stove cooking, and electricity generation [6]. Coal consumption is also important for development in emerging economies. For example, in China, coal is currently dominating the energy consumption market by an impressive ratio of nearly 69%. Industrial coal



consumption from 2008 to 2035 has been estimated to grow by 67% in China and 94% in India. Countries whose energy landscape is dominated by coal are the highest emitters of CO<sub>2</sub>. For example, China, the United States and India were the top three CO<sub>2</sub> emitters in 2008 [7].

Given the aforementioned drawbacks of renewable energy and the current global economic dependence on coal, especially in developing economies, it is clear that coal will remain important on the global energy scale in the near future. It would be beneficial, in terms of the environment and economics, to have a coal powered process that produces little or no CO<sub>2</sub> emissions. With such a coal-fired plant/process in place, coal can be an environment friendly energy producing asset. This work aims to find novel ways of reducing CO<sub>2</sub> emissions from a traditional coal-fired power plant.

A method already in place to assuage the environmental side effects of coal is the integration of carbon capture and storage technology with traditional coal power plants. Amine scrubbing is a promising technology nearly applicable to industrial use. But aqueous amines operation is costly while solid amines technology is less developed [8]. Another disadvantage is that, although carbon capture technology, namely amine scrubbing, is used in existing coal-fired power plants and syngas power plant [9,10], this integration maintains a CO<sub>2</sub> capture of 90% and the captured product, more often than not is sequestered and has no commercial value. These shortcomings can be eliminated if produced CO<sub>2</sub> is converted on spot into high market value carbon-containing chemicals. In this case, there will be no CO<sub>2</sub> emissions and the sale of the produced chemical can yield economic benefits. This work proposes the production of a useful chemical (formic acid) from a coal-fired process without the generation of GHGs (carbon dioxide).

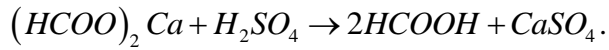
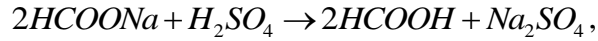
A formic acid molecule has a structure of one carboxyl group and a hydrogen atom connecting with the carbon atom of the carboxyl group through a C-H polar covalent bond. Thus, for its production, a stream of hydrogen and CO<sub>2</sub> will suffice. Formic acid has various applications in the real world: it plays an important role in the production of preservatives, with the carboxyl group functioning as an antibacterial agent in livestock feed, leather production, and cleaning [11,12]; in addition, formic acid also plays an important part in household and industrial cleaning, oilfield drilling and gas exploration [12]. The market value of formic acid is estimated to reach USD 618.809 million by 2019, growing at a compound annual growth rate of 4.9%, from 2014 to 2019 [13].

Formic acid is produced commercially via two main routes: methyl formate hydrolysis and production from formates [14]. In methyl formate hydrolysis (e.g. Kemira–Leonard Process), carbonylation is carried out at about 4 MPa and approximately 80°C. Hydrolysis is carried out in two reactors under two different conditions. The formation reaction is shown below:

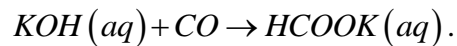
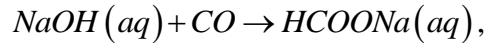


The hydrolysis reactor discharge contains formic acid and water which is brought to atmospheric pressure. The formic acid produced is then dehydrated by distillation. Depending on the operating conditions and the anticipated purity, various distillation sequences are employed to yield formic acid with purities ranging from 85 – 98% [14].

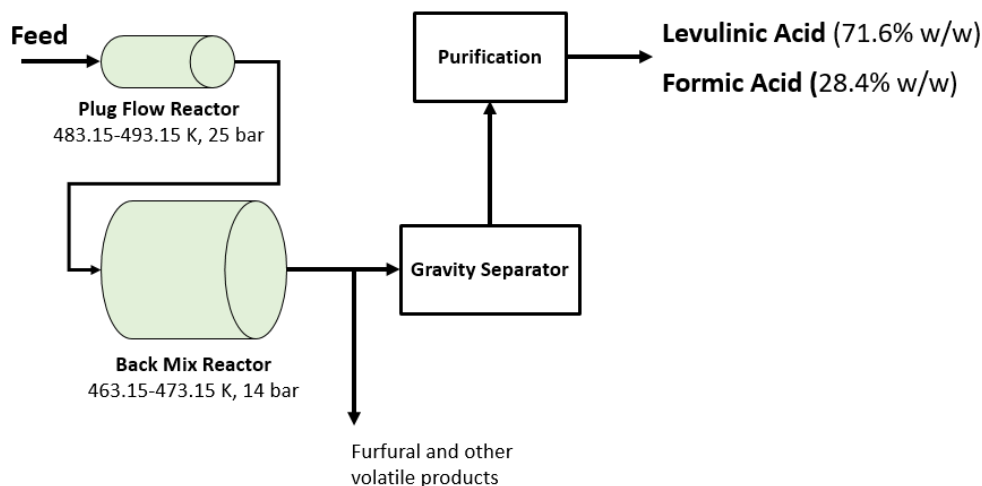
Formic acid can also be produced by increasing the acidity of a format solution:



One way of synthesizing formate salt is using the reaction of CO and alkali aqueous solution:



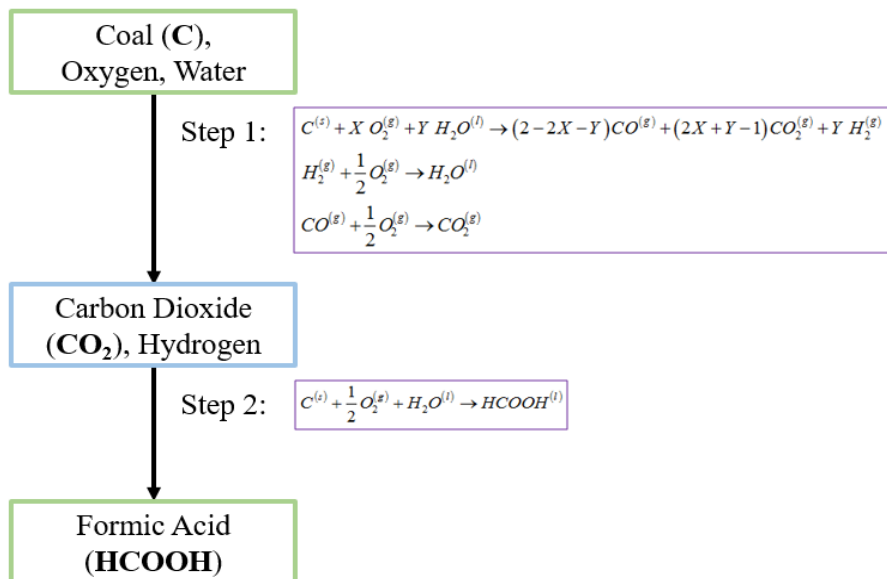
Other formic acid production methods include the biofine process. As shown in **Error! Reference source not found.**, lignocellulosic feedstock is initially shredded and mixed with recycled dilute sulphuric acid. Then it is feed to the biofine process which has two distinct acid-catalyzed stages. The first reactor, preferably a plug flow reactor with a small diameter, carries out the first order hydrolysis reaction at 483.15-493.15 K and 25 bar with a short residence time. Products are continuously removed. The second reactor favors the first order reaction sequence leading to the production of levulinic acid, due the complete mixed condition. The operating condition of the second reactor is 463.15-473.15 K and 14 bar. Furfural and other volatile products are removed while the tarry mixture of levulinic acid and residues are passed to a gravity separator. The insoluble mixture is dehydrated by heating and is purified as levulinic acid up to a purity of 98%. Formic acid takes up 28.4% as a byproduct of levulinic acid [15].



**Figure 1. The bio-fine Process for the production of formic acid**

Hydrogenation of carbon dioxide is another method of synthesizing formic acid and this can be done under various conditions. One operating condition is the use of water-soluble rhodium catalysts and the provision of an aqueous solution environment at room temperature and 40.52 bar. According to the experimental data, formic acid concentrations were up to  $3.63 \text{ mol/dm}^3$  and the turnover numbers were up to 3439 [16].

The formic acid production method put forward in this work is a two-step chemical process shown in **Figure 2** which involves a different  $\text{CO}_2$  hydrogenation condition [17]. The first step generates hydrogen and  $\text{CO}_2$  with the help of two reactors and the second step employs one reactor to carry out the  $\text{CO}_2$  hydrogenation. The overall process employs coal, oxygen, and water as raw materials, while the second step produces formic acid by the reaction of  $\text{CO}_2$  and  $\text{H}_2$ . The whole process generates zero net carbon dioxide emissions.



**Figure 2. A Simple Schematic of the proposed Two-step Process**

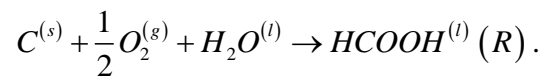
In 2011, Pena Lopez & Manousiouthakis, designed a process flowsheet co-producing hydrogen and formic acid from natural gas, oxygen, and water. In their proposed process, hydrogen is generated through steam methane reforming (SMR), while CO<sub>2</sub> is produced through combustion of natural gas as well as SMR. Using generated H<sub>2</sub> and CO<sub>2</sub>, a reactor is employed to carry out CO<sub>2</sub> hydrogenation to produce formic acid. The whole process is energetically self-sufficient, which by definition is a steady-state open system whose net shaft work and heat transfer is non-positive (i.e. work and heat transferred from the system to the surroundings) [18]. This work is built on such concept by seeking out a process that produces formic acid using coal as feedstock.

In the following sections, first, an overall reaction with a thermodynamic analysis is carried out and its reaction cluster consisting of four reactions is presented. The thermodynamic analysis ensures the thermodynamic feasibility of the overall reaction and predict its energetically self-sufficient behaviors. Next a process flowsheet and its individual sections are described in detail.

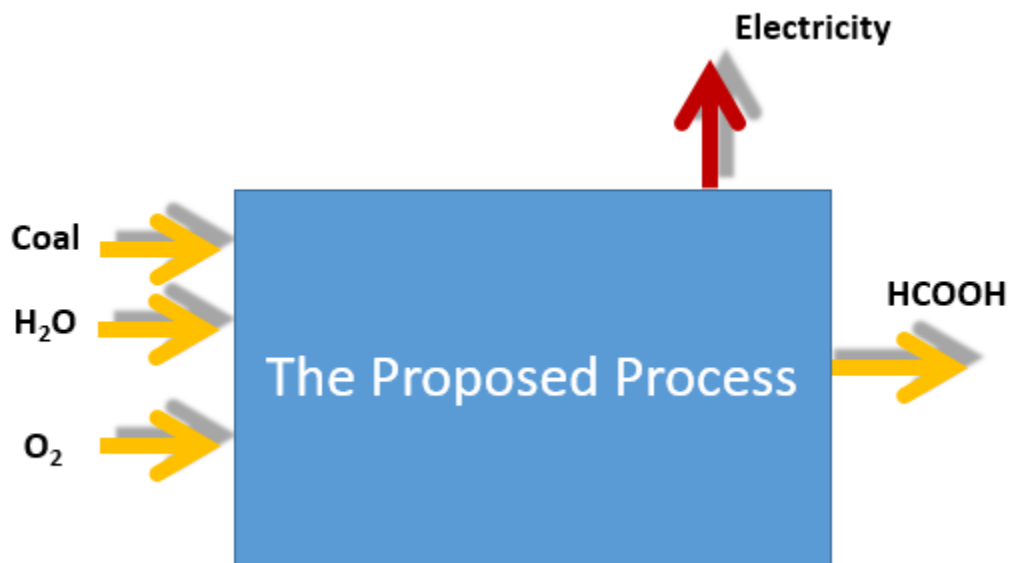
Finally, a heat and power integration and an economic analysis of the proposed process are performed.

## 2. Thermodynamic/Energetic Self-Sufficiency Analysis of Proposed System

The inlet of the proposed system is composed of coal, water, and oxygen and the outlet of the system is formic acid. The overall reaction (R) is shown below:



Note that (R) is not an actual existing reaction. **Figure 3** shows a schematic of the process.



**Figure 3. Schematic of process for co-production of formic acid and electricity from coal**

The concept of energetic self-sufficiency [18] is reviewed below:

*Definition:* Let  $\Omega$  be a steady-state open system with inlets in  $S_I$ , outlets in  $S_O$ , no heat transferred from the surroundings to the system, heat possibly transferred from the system to the surroundings  $\dot{Q}_0 \leq 0$ , at the uniform surroundings temperature  $T_0$ , and the system's net shaft work to be non-positive  $\sum_{j \in S_W} \dot{W}_{s,j} \leq 0$ . Such a system is called energetically self-sufficient.

Mathematically, an open well delimited system satisfying 
$$\sum_{i \in S_I} \dot{m}_i - \sum_{i \in S_O} \dot{m}_i = 0 \quad \text{Equation 1}$$

$$\sum_{i \in S_I} \sum_{j \in S_C} v_{j,k} \frac{x_{i,j}}{M_j} \dot{m}_i - \sum_{i \in S_O} \sum_{j \in S_C} v_{j,k} \frac{x_{i,j}}{M_j} \dot{m}_i = 0 \quad \forall k \in S_E \quad \text{Equation 2}$$

$$\sum_{j \in S_W} \dot{W}_{s,j} = T_0 \cdot \dot{S}_G - \left( \sum_{i \in S_I} (H_i - T_0 \cdot S_i) \dot{m}_i - \sum_{i \in S_O} (H_i - T_0 \cdot S_i) \dot{m}_i \right) \leq 0 \quad \text{Equation 3}$$

through **Error! Reference source not found.** is said to be energetically self-sufficient [19]:

$$\sum_{i \in S_I} \dot{m}_i - \sum_{i \in S_O} \dot{m}_i = 0 \quad \text{Equation 1}$$

$$\sum_{i \in S_I} \sum_{j \in S_C} v_{j,k} \frac{x_{i,j}}{M_j} \dot{m}_i - \sum_{i \in S_O} \sum_{j \in S_C} v_{j,k} \frac{x_{i,j}}{M_j} \dot{m}_i = 0 \quad \forall k \in S_E \quad \text{Equation 2}$$

$$\sum_{j \in S_W} \dot{W}_{s,j} = T_0 \cdot \dot{S}_G - \left( \sum_{i \in S_I} (H_i - T_0 \cdot S_i) \dot{m}_i - \sum_{i \in S_O} (H_i - T_0 \cdot S_i) \dot{m}_i \right) \leq 0 \quad \text{Equation 3}$$

$$\dot{Q}_0 = T_0 \cdot \left( \sum_{i \in S_I} S_i \dot{m}_i - \sum_{i \in S_O} S_i \dot{m}_i \right) - T_0 \cdot \dot{S}_G \leq 0, \dot{S}_G \geq 0 \quad \text{Equation 4}$$



where  $S_I$  and  $S_O$  are the sets of all streams of inlet and outlet,  $\dot{m}_i$  is the mass flowrate of the  $i$ -th stream,  $S_C$  is the set of all chemical species comprising the system,  $v_{j,k}$  is the stoichiometric coefficient of the constituent element  $k$  in the formation reaction of the  $j$ -th chemical species,  $M_j$  is the molecular weight of the  $j$ -th chemical species,  $x_{i,j}$  is the mass fraction of the  $j$ -th chemical species in the  $i$ -th stream,  $S_E$  is the index set of constituent elements,  $\dot{W}_{s,j}$  is rate of shaft work consumed by the  $j$ -th source in the system,  $T_0$  is the reference temperature,  $\dot{S}_G$  is the total rate of entropy generation due to irreversibilities both within the system's control volume and in the heat transfer across temperature differences between the control volume and its surroundings,  $\Delta\dot{H}_s(T_0)$  and  $\Delta\dot{G}_s(T_0)$  respectively stand for the system's enthalpy and Gibbs free energy change rates at  $T_0$  (298.15 K),  $H_i$ ,  $G_i$ , and  $S_i$  are the specific mass enthalpy, Gibbs free energy and entropy respectively of the  $i$ -th stream at its temperature and pressure conditions  $T_i$  and  $P_i$  [18].

$$\sum_{i \in S_I} \dot{m}_i - \sum_{i \in S_O} \dot{m}_i = 0 \quad \text{Equation 1}$$

$$\sum_{i \in S_I} \sum_{j \in S_C} v_{j,k} \frac{x_{i,j}}{M_j} \dot{m}_i - \sum_{i \in S_O} \sum_{j \in S_C} v_{j,k} \frac{x_{i,j}}{M_j} \dot{m}_i = 0 \quad \forall k \in S_E \quad \text{Equation 2}$$

$$\sum_{j \in S_W} \dot{W}_{s,j} = T_0 \cdot \dot{S}_G - \left( \sum_{i \in S_I} (H_i - T_0 \cdot S_i) \dot{m}_i - \sum_{i \in S_O} (H_i - T_0 \cdot S_i) \dot{m}_i \right) \leq 0 \quad \text{Equation 3}$$

defines the mass balance of the all the inlet streams and all the outlet streams within the whole system. **Error! Reference source not found.** guarantees the element balance for every chemical element in the streams, by comparing the molar flowrates of inlet and outlet streams for each

element. **Error! Reference source not found.** stipulates no heat entry to the system. **Error! Reference source not found.** guarantees no external power is required from the environment. The term,  $T_0 \cdot \dot{S}_G = L\dot{W}$ , is also known as the “rate of lost work” for a system producing work and the term,  $H_i - T_0 \cdot S_i = B_i$ , is also known as the “thermodynamic availability” [20]. If  $T_i = T_0$   $\forall i \in S_I \cup S_O$ , then  $H_i - T_0 \cdot S_i = G_i$   $\forall i \in S_I \cup S_O$ , where  $G_i$  is the specific Gibbs free energy at the temperature and pressure conditions  $T_0$  and  $P_i$   $\forall i \in S_I \cup S_O$ . This also means  $B_i = G_i$ , if  $H_i$  and  $S_i$  are evaluated at  $T_0$ . In order to realize energetically self-sufficiency, the necessary condition follows:

$$\left\{ \begin{array}{l} \sum_{i \in S_I} H_i \dot{m}_i - \sum_{i \in S_O} H_i \dot{m}_i \geq 0 \\ \sum_{i \in S_I} B_i \dot{m}_i - \sum_{i \in S_O} B_i \dot{m}_i = \sum_{i \in S_I} (H_i - T_0 \cdot S_i) \dot{m}_i - \sum_{i \in S_O} (H_i - T_0 \cdot S_i) \dot{m}_i \geq 0 \end{array} \right\}.$$

The availability flow rate of the inlet streams is greater than that of the outlet streams, causing the above inequalities are consistent with heat flowing from the system to the surroundings and work being generated by the system. Considering the fact that if  $\{T_i = T_0 = 298.15 \text{ K} \wedge P_i = P_0 = 1 \text{ bar}\}$   $\forall i \in S_I \cup S_O$ , the above necessary condition becomes:

$$\left\{ \begin{array}{l} \Delta \dot{H}_s(T_0, P_0) \triangleq \sum_{i \in S_I} H_i \dot{m}_i - \sum_{i \in S_O} H_i \dot{m}_i \geq 0 \\ \Delta \dot{G}_s(T_0, P_0) \triangleq \sum_{i \in S_I} G_i \dot{m}_i - \sum_{i \in S_O} G_i \dot{m}_i = \sum_{i \in S_I} (H_i - T_0 \cdot S_i) \dot{m}_i - \sum_{i \in S_O} (H_i - T_0 \cdot S_i) \dot{m}_i \geq 0 \end{array} \right\}.$$

A balanced, overall chemical reaction is considered for the system, in order to quantify the energetically self-sufficient conditions introduced above:

$$\sum_{j \in S_C} \mu_j C_j = 0;$$

where positive component coefficients ( $\mu_j > 0$ ) stand for the system products, negative component coefficients ( $\mu_j < 0$ ) stand for the system reactants, and  $C_j$  designate the system species.

The equation  $\sum_{i \in S_I} \frac{1}{|\mu_j|} \frac{1}{M_j} x_{ij} \dot{m}_i = \sum_{i \in S_O} \frac{1}{|\mu_j|} \frac{1}{M_j} x_{ij} \dot{m}_i \quad \forall j \in S_C$  leads to the following definition of

a normalized molar flow rate for the system:

$$\dot{\eta} = \sum_{i \in S_I} \frac{1}{|\mu_j|} \frac{1}{M_j} x_{ij} \dot{m}_i = \sum_{i \in S_O} \frac{1}{|\mu_j|} \frac{1}{M_j} x_{ij} \dot{m}_i \quad \forall j \in S_C .$$
 Accordingly, the molar flow rate for each

species is  $|\mu_j| \dot{\eta} \quad \forall j \in S_C$ .

Then the above necessary and sufficient, and necessary conditions for energetical self-sufficiency become respectively:

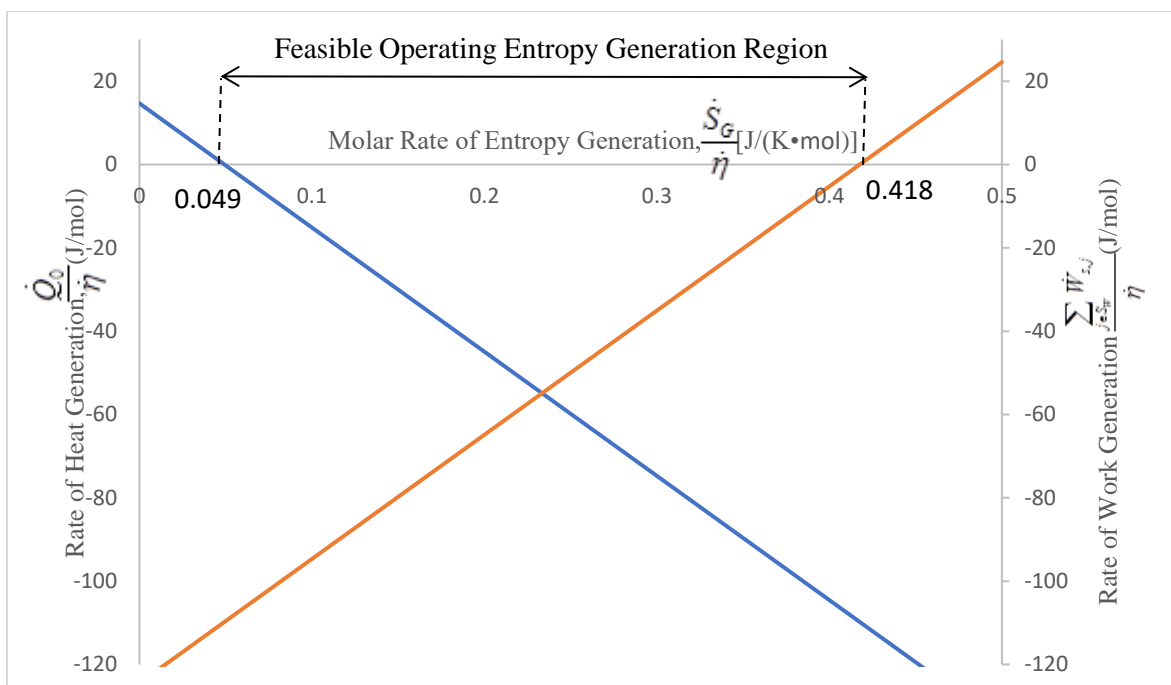
$$\left. \begin{array}{l} \frac{\dot{Q}_0}{\dot{\eta}} = -T_0 \sum_{j \in S_C} s_j \mu_j - T_0 \cdot \frac{\dot{S}_G}{\dot{\eta}} \leq 0, \quad \frac{\dot{S}_G}{\dot{\eta}} \geq 0 \\ \frac{\sum_{j \in S_W} \dot{W}_{s,j}}{\dot{\eta}} = T_0 \frac{\dot{S}_G}{\dot{\eta}} + \sum_{j \in S_C} (h_j - T_0 s_j) \mu_j \leq 0 \\ \sum_{j \in S_C} h_j \mu_j \leq 0, \quad \sum_{j \in S_C} (h_j - T_0 s_j) \mu_j \leq 0 \end{array} \right\} \text{Equation 5.}$$

The overall reaction (R) is then assessed to see if it is energetically self-sufficient when the system's streams enter and leave at  $T_0 = 298.15\text{ K}$ ;  $P_0 = 1\text{ bar}$ . This would be explored using standard state properties (when ideal gas and ideal mixtures are assumed) [21] and equation of state properties. Both scenarios are achieved using the ideal gas and PRSV equations of state of UNISIM respectively whose values are tabulated in **Table 1**. Substitution of the values from **Table 1** into **Equation 5** yield **Figure 4** and **5** for the standard state and equation of state respectively.

Species	$\Delta h_{f,i}^0$ kJ/mol	UniSim $h_i$ kJ/mol	$\Delta g_{f,i}^0$ kJ/mol	UniSim $g_i$ kJ/mol	$\Delta s_{f,i}^0$ kJ/(mol · K)	UniSim $s_i$ kJ/(mol · K)
C <sup>s</sup>	0.0	0.0038	-	-1.5	0.0057	0.0051
CO <sup>g</sup>	-110.5	-110.6	-137.2	-158.1	0.1977	0.1592
CO <sub>2</sub> <sup>g</sup>	-393.5	-393.8	-394.4	-445.2	0.2138	0.1725
HCOOH <sup>l</sup>	-425.0	-402.6	-361.4	-423.5	0.1290	0.0701
H <sub>2</sub> <sup>g</sup>	0.0	-0.0003	-	-36.7	0.1307	0.1231
H <sub>2</sub> O <sup>l</sup>	-285.8	-285.6	-237.1	-302.1	0.0700	0.0554
O <sub>2</sub> <sup>g</sup>	0.0	-0.0109	-	-43.3	0.2052	0.1451

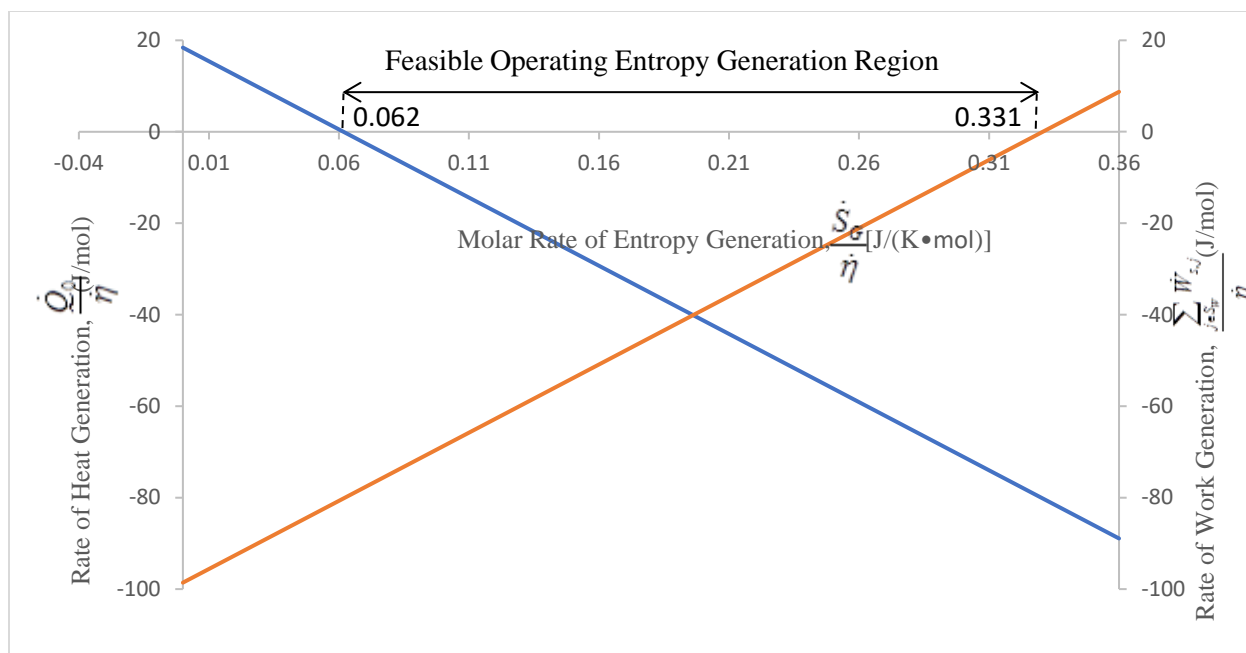
(g) = gas state, (l) = liquid, (s) = solid.

**Table 1. Standard Molar Enthalpies, Gibbs Molar Free Energy, and Standard Molar Entropies**



**Figure 4. Energetic Self-sufficiency feasible region in  $(\frac{\dot{S}_G}{\dot{\eta}}, \frac{\dot{Q}_0}{\dot{\eta}} / \frac{\sum_{j \in S_W} \dot{W}_{s,j}}{\dot{\eta}})$  space for standard state**

As can be seen, the overall reaction is feasible within a certain range of rate entropy generation values. This range is between 0.049-0.418 kJ/(K•mol) for the standard condition values and it guarantees the production of formic acid as well as heat/power.



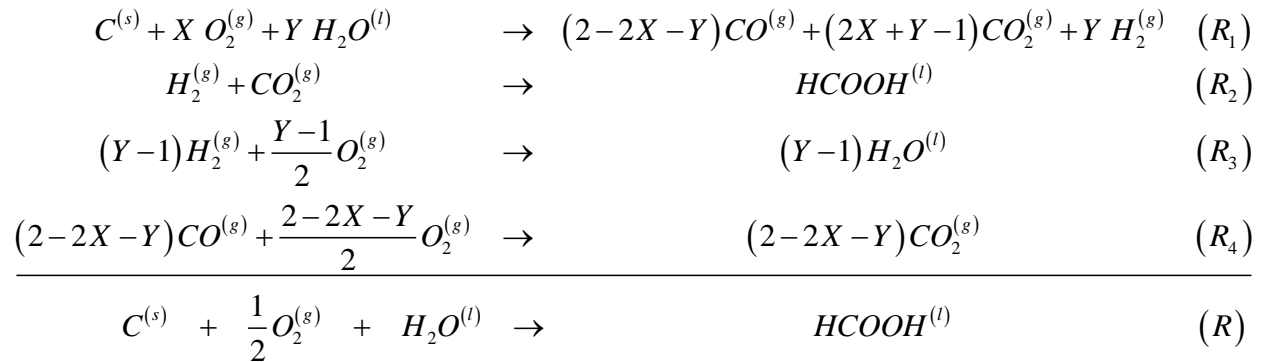
**Figure 5. Energetic Self-sufficiency feasible region in  $(\frac{\dot{S}_G}{\dot{\eta}}, \frac{\dot{Q}_0}{\dot{\eta}} / \frac{\sum_{j \in S_w} \dot{W}_{s,j}}{\dot{\eta}})$  space for equation of state**

As can be seen, the overall reaction is feasible within a certain range of rate entropy generation values. This range is between 0.063-0.329 kJ/(K•mol) for the equation of state based values and it guarantees the production of formic acid as well as heat/power.

### 3. Realization of Proposed Formic Acid and Power Co-Production Process

A novel chemical process realizing the overall reaction (R) is developed. Since (R) cannot be realized within one single step, its realization is fulfilled by a cluster of feasible reactions [22-25], also frequently referred to as a Solvay cluster, whose overall reaction gives the desired

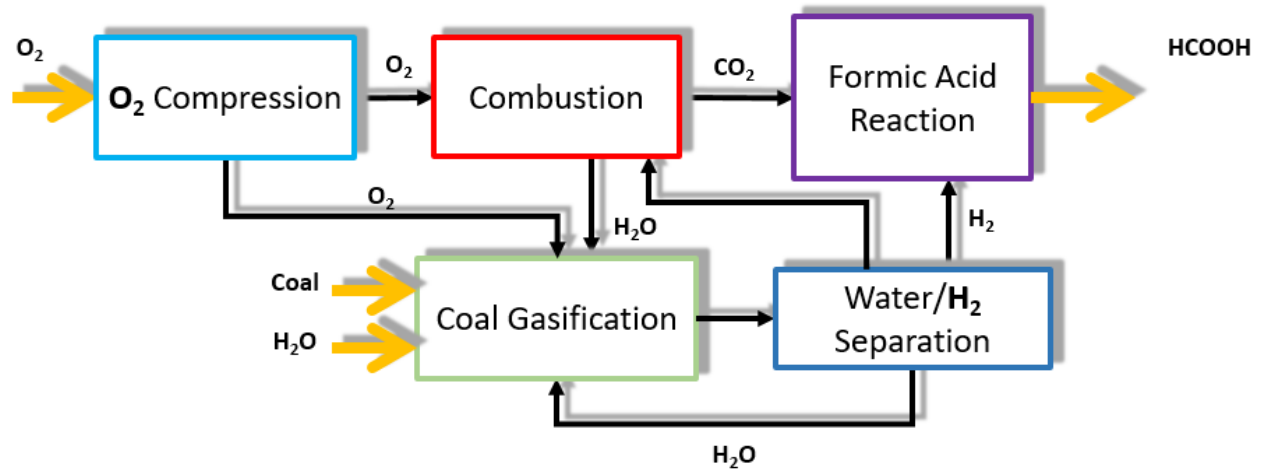
reaction (R). The novel reaction cluster and its feasible, constitutive reactions are shown in **Error! Reference source not found.**:



**Figure 6. Reaction cluster generating formic acid from coal**

The reaction cluster consists of the following feasible reactions: coal gasification to syngas (R1), CO<sub>2</sub> hydrogenation to formic acid (R2), hydrogen combustion (R3), and carbon monoxide combustion (R4).

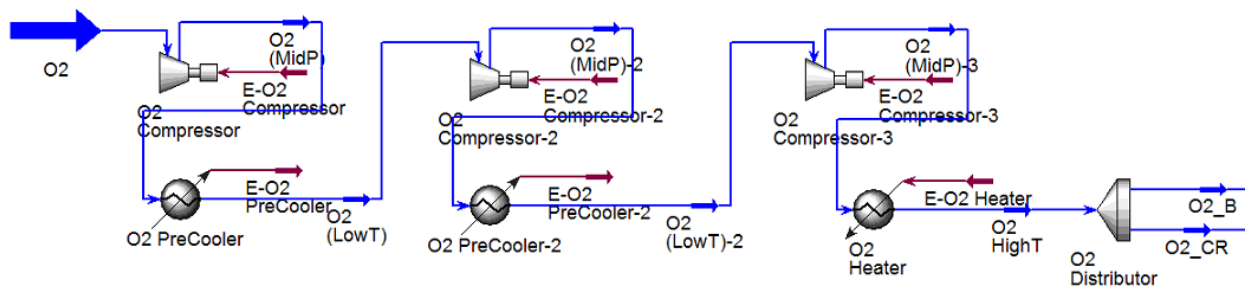
The reaction cluster described above establishes the conceptual framework for realizing the overall reaction (R) using well-developed technologies, such as combustion, coal gasification, gas compression, supercritical fluid pumping, hydrogen separation using pressure swing adsorption, and formic acid production from CO<sub>2</sub> and H<sub>2</sub>. A detailed process description is provided below. To streamline the exposition, five process subsystems are considered. Those are: Oxygen Compression Subsystem, Coal Gasification Subsystem, Water/Hydrogen Separation Subsystem, Combustion Subsystem, Formic Acid Reaction Subsystem. The conceptual relations among those subsystems are shown in **Error! Reference source not found.**, followed by detailed description of each subsystem.



**Figure 7. Summary of overall process realization**

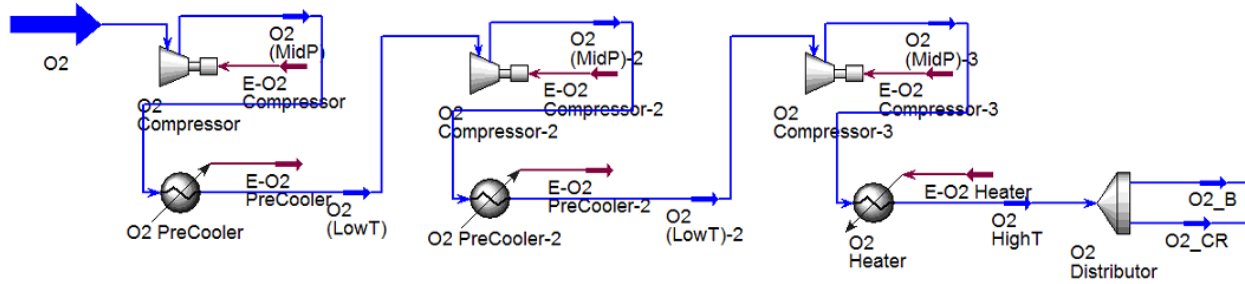
### 3.1. Oxygen Compression Subsystem

The Oxygen Compression subsystem is shown in



**Figure .** Pure oxygen at 298.1 K, 1.013 bar is compressed through a set of compressors and coolers to 403 K, 53 bar. Oxygen is then heated to 1220 K and distributed to the Coal Gasification and Combustion subsystems.

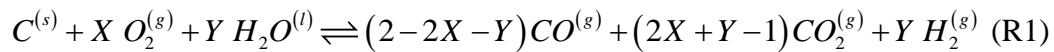




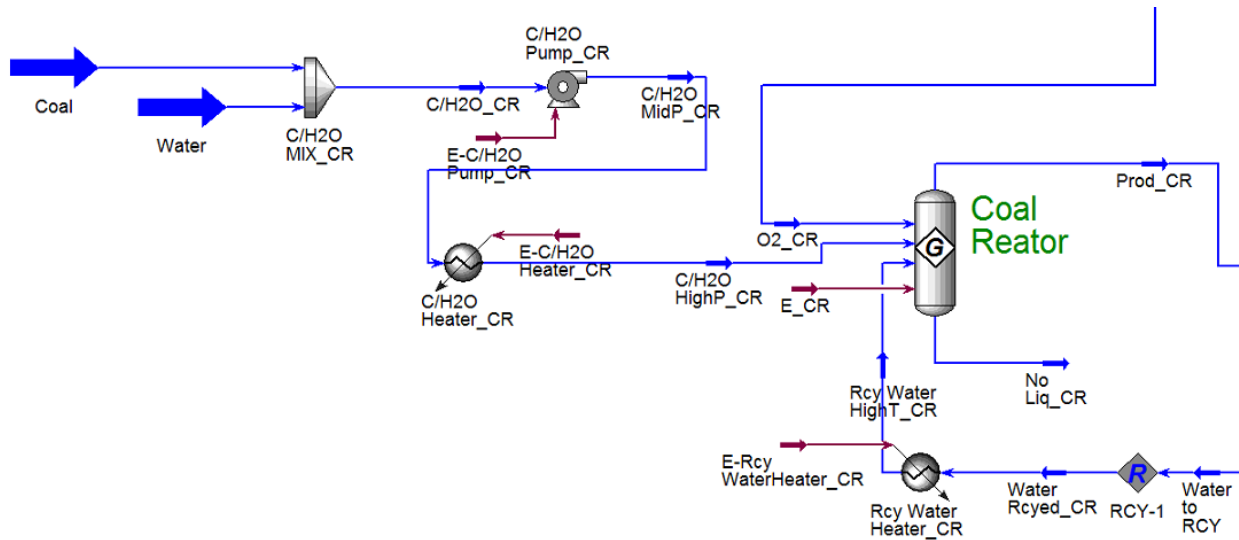
**Figure 8. Oxygen Compression subsystem**

### 3.2. Coal Gasification Subsystem

Coal gasification usually takes place within 810 K-1093 K and 1 bar-71 bar [26]. In this work, coal and water at 298.1 K, 1.013 bar are mixed into a slurry. The slurry is then compressed to 53 bar through a pump, and heated to 1220 K. It is then fed into a coal gasification reactor together with the previously mentioned oxygen stream at the same condition. Extracted water (310 K, 53 bar) from later subsystems is reheated to 1220 K and recycled to the coal gasification reactor. The reaction temperature is 1230 K and the reaction follows reaction (R1).



The gasification product at 1230 K and 53 bar is a vapor whose composition is 57% water, 23% H<sub>2</sub>, 12% CO<sub>2</sub>, and 8% CO. The vapor product is later sent to the Water/Hydrogen Separation subsystem. The subsystem is shown in **Figure** .



**Figure 9. Coal Gasification subsystem**

### 3.3. Water/Hydrogen Separation Subsystem

The product from the aforementioned coal gasification reactor is cooled to 310 K and the cool stream is introduced into a phase separator. Water is recycled while the dry vapor outlet is fed into a hydrogen pressure swing adsorber. Hydrogen recovery is assumed to be 90% while its purity is 99.99%. The PSA inlet is at 53 bar. The pure hydrogen end is at 53 bar while the PSA off gas is at 5.03 bar [9]. The PSA off gas later flows into the Combustion subsystem. The Water/Hydrogen Separation subsystem is presented as

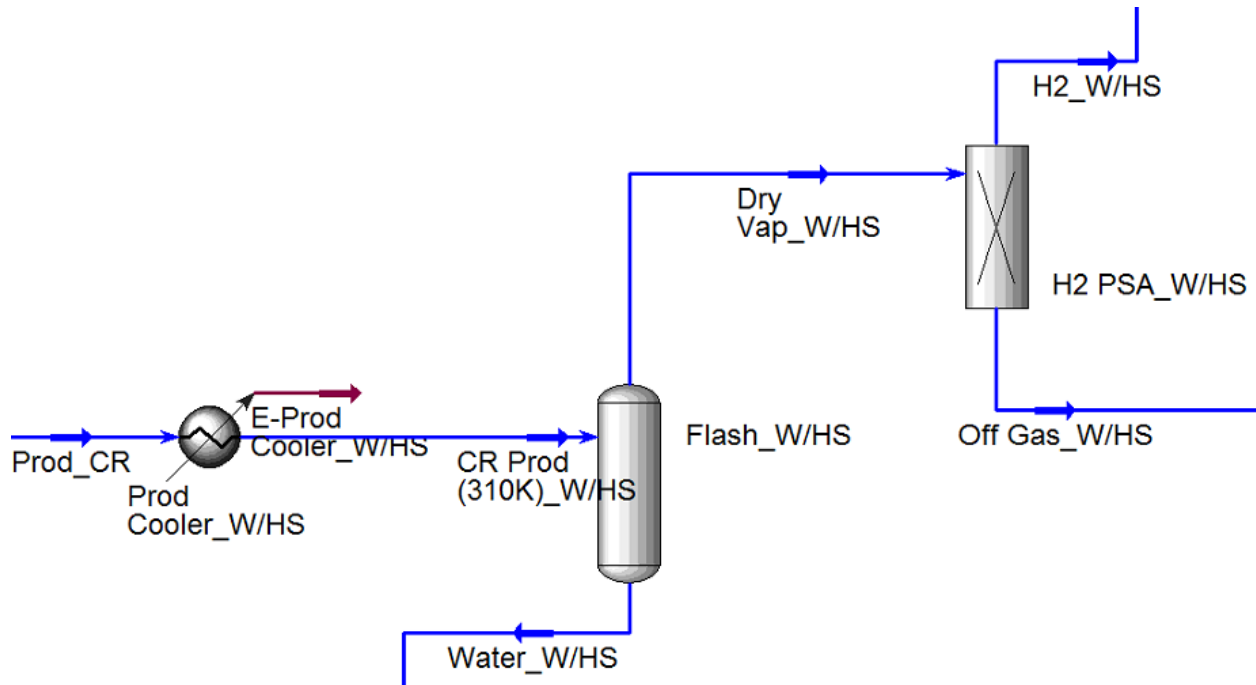


Figure .

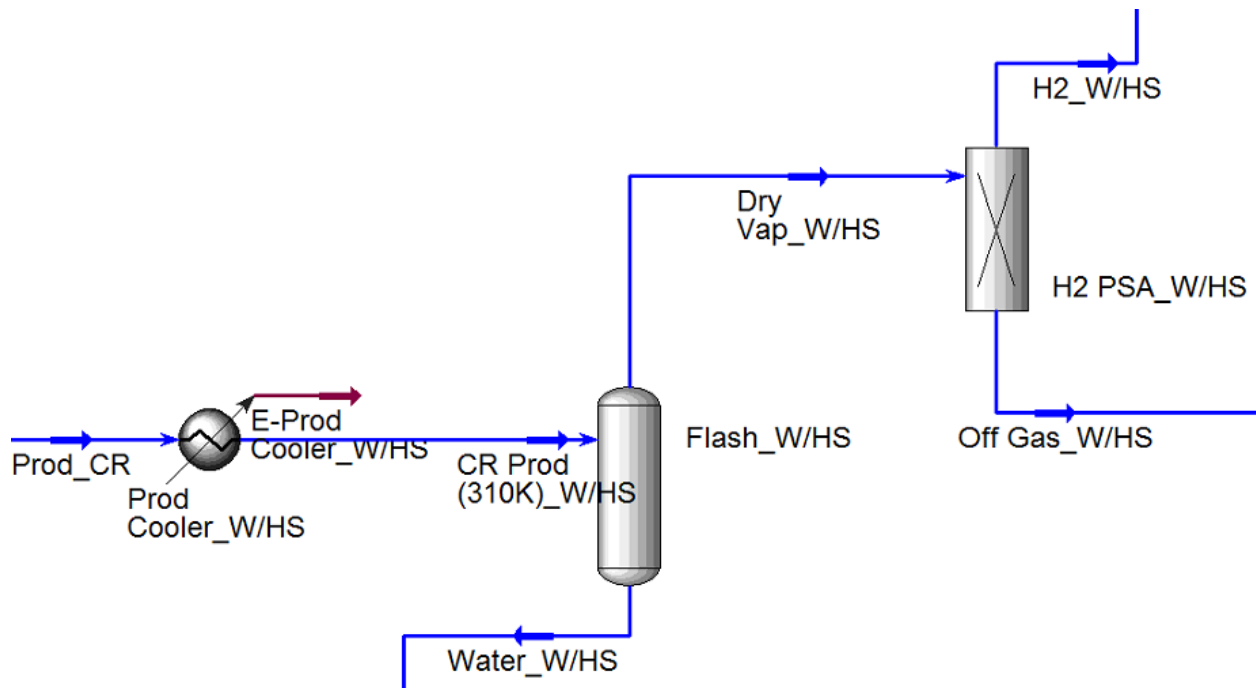
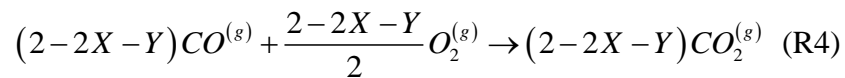
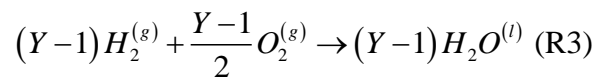


Figure 10. Water/Hydrogen Separation subsystem

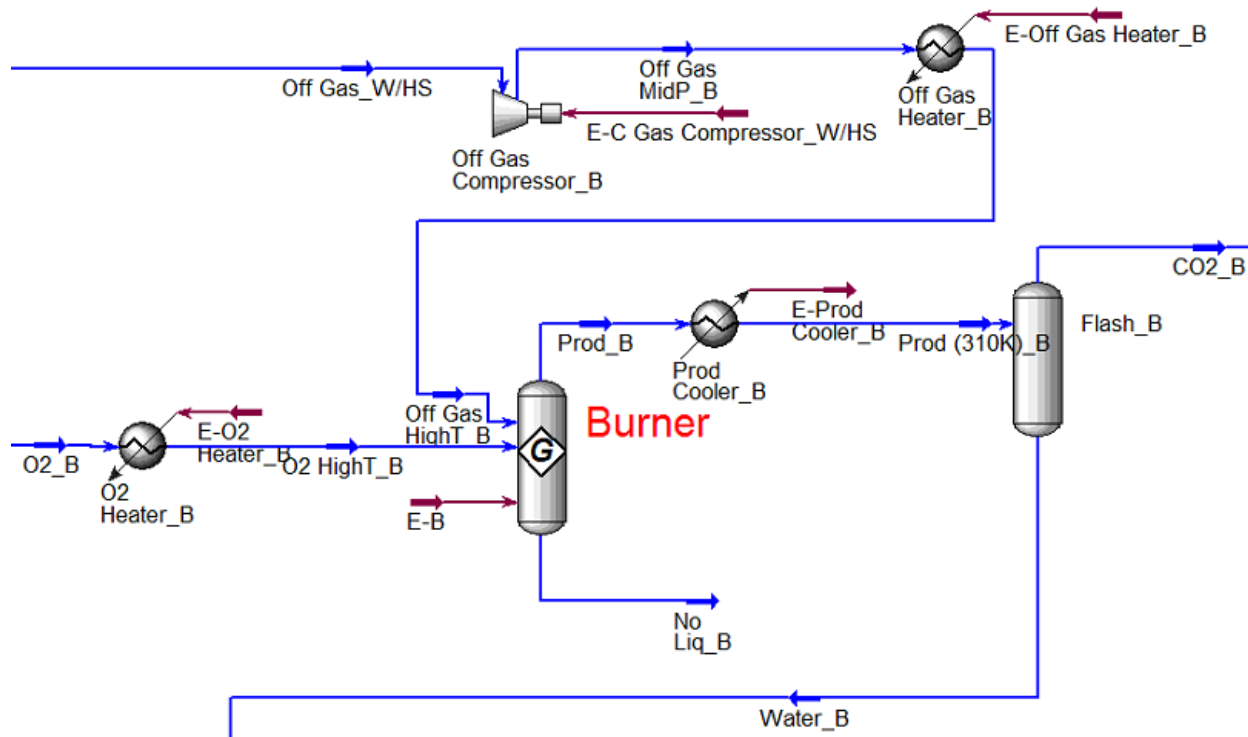
### 3.4. Combustion Subsystem

The off-gas stream from PSA is compressed to 53 bar and heated to 1240 K. Off gas and oxygen from the oxygen compression subsystem are fed into a burner at 1240 K, 53 bar.

Combustion is assumed to take place at 1250 K. The combustion includes reactions (R3) and (R4) below:



The combustion product at 1250 K, 53 bar is cooled to 310 K and goes through a phase separator. Water is recycled back to the coal gasification reactor while the dry gas consists mostly of CO<sub>2</sub>. This dry CO<sub>2</sub> stream is sent to the Formic Acid Reaction subsystem. The combustion subsystem is shown in **Figure** .

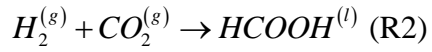


**Figure 11. Combustion subsystem**

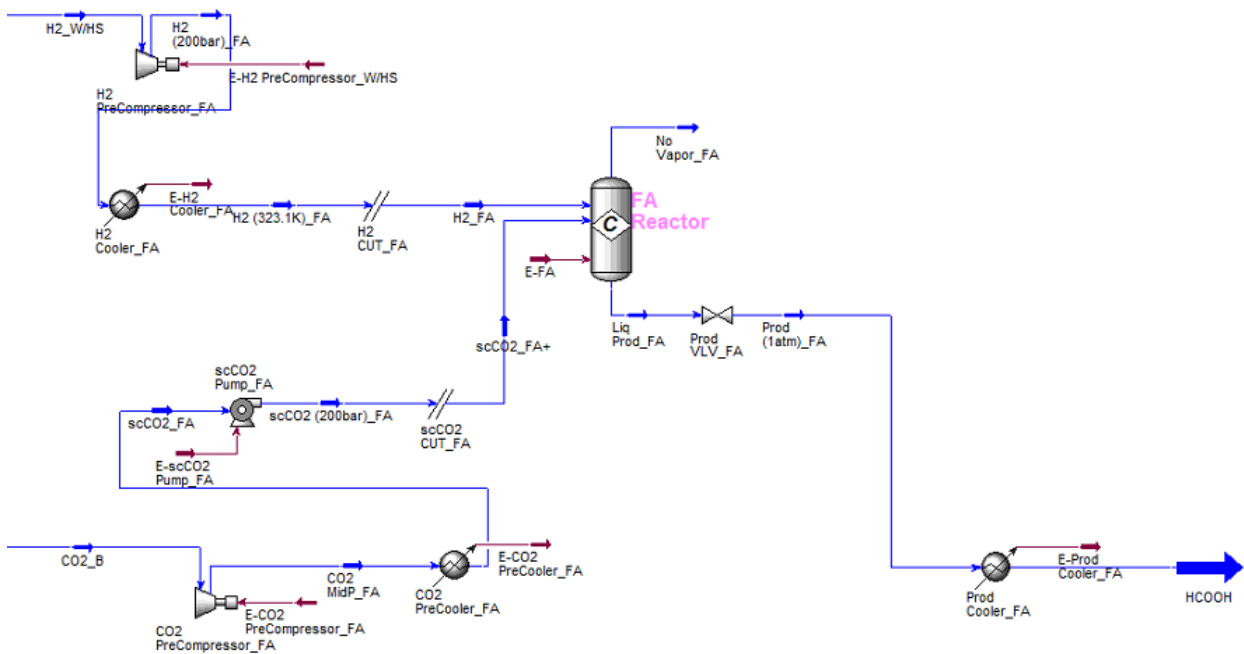
### 3.5. Formic Acid Reaction Subsystem

Pure hydrogen is compressed to 200 bar and heated to 323.1 K. CO<sub>2</sub> is pre-compressed to 131.7 bar and cooled to 310 K in order to obtain supercritical CO<sub>2</sub>. A compressor is then employed to compress supercritical CO<sub>2</sub> to 200 bar. The mixture is then sent to a formic acid reactor to produce formic acid. The reactor is modelled as previously mentioned in the introduction section [17]. The feed consisting of hydrogen and supercritical CO<sub>2</sub> enters an ionic phase which is full of catalyst and stabilizing base. The operating temperature is 50 °C (323.1 K), while the pressure is 200 bar [17]. The reactor product consists of supercritical CO<sub>2</sub> and formic acid. It is depressurized so that pure formic acid liquid is collected and vapor CO<sub>2</sub> can be recycled. CO<sub>2</sub> is then

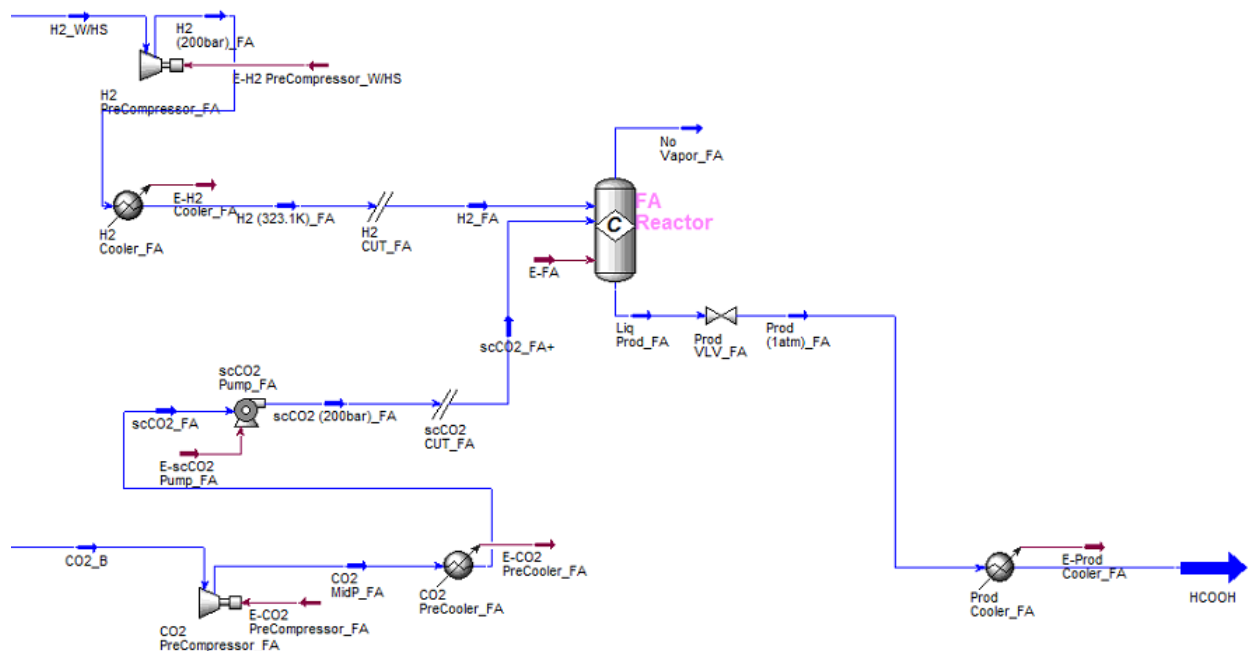
recompressed to 200 bar and fed to the formic acid reactor. The formic acid reaction (R2) is modelled in a conversion reactor:



Formic acid (95.95% purity) exits the conversion reactor at 73 bar. It is depressurized to 1.013 bar and cooled to 310 K after which it exits the flowsheet as a saleable product.



**Figure** shows the formic acid subsystem.



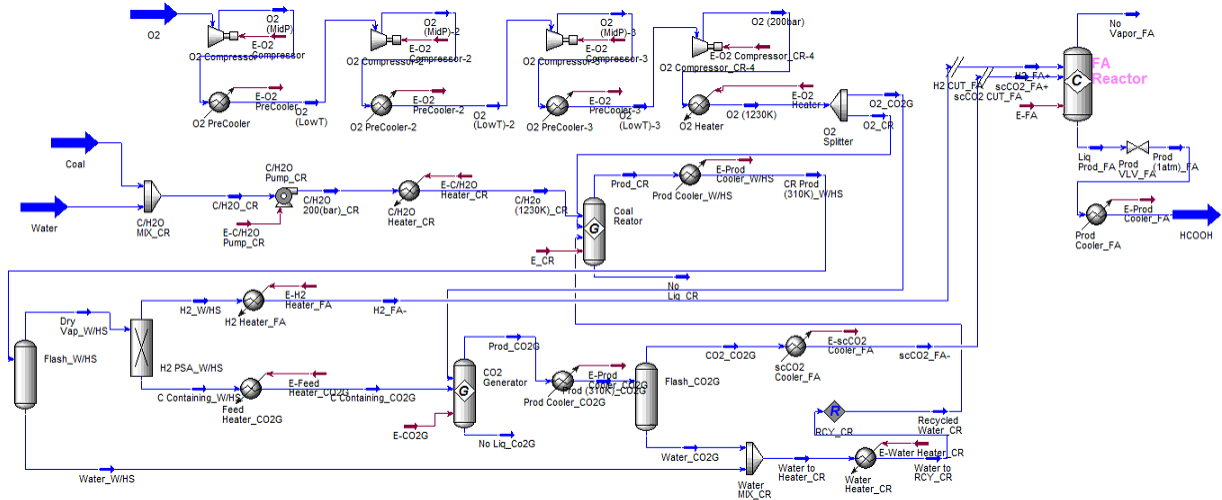
**Figure 12. Formic Acid Reaction Subsystem**

## 4. Flowsheet Simulation of Reaction Cluster Realization

After connecting all aforementioned subsystems, a converged flowsheet is generated using the software UniSim Design R443. The Peng-Robinson-Stryjeke-Vera Equation of state is used to simulate the coal gasification and combustion sections of the flowsheet, while for the formic acid synthesis sections, the van Laar liquid activity coefficient model coupled with an ideal gas model for the vapor phase is employed. The feed streams are coal, oxygen, and water at 1.013 bar, 298.1 K and the product is formic acid only at the same conditions. Two Gibbs reactors act as the

gasification reactor and a combustor, while a conversion reactor carries out the formic acid reaction. A schematic of the overall process, which combines **Figures 8 – 12**, is presented in

**Figure 1.**



**Figure 1. Overall Process Simulation in UniSim® Design**

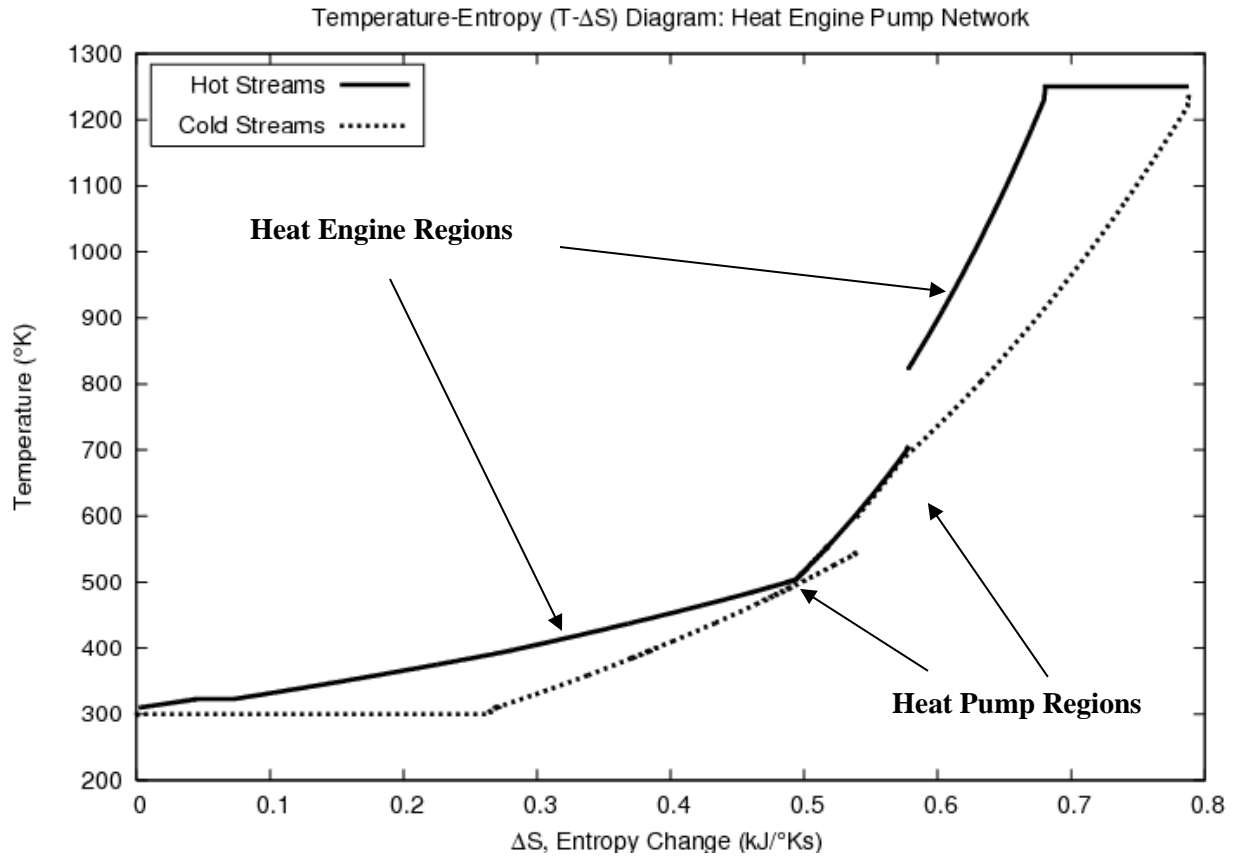
The following assumptions are made during the flowsheet’s design:

1. All input feeds to the flowsheet are considered pure.
2. Pressures are considered constant in heat exchange devices (heaters and coolers) utilized for temperature changing operations.
3. Adiabatic efficiencies of all turbine/expanders and pump/compressors are fixed at 85%.



## 5. Heat and Power Integration of Proposed Flowsheet for the Co-Production of Formic Acid and Electricity

Heat and power integration uses a mathematical approach to solve the minimum hot/cold/electric utility cost problem in a heat exchange network [27,28]. In the heat exchange network, an optimal integration of heat exchangers, heat engines and heat pumps is approached if the process streams flow rates, their inlet and outlet temperatures, and the inlet and outlet temperatures of hot/cold utility streams are all known [27]. Both streams with sensible and latent heat supply/demand requirements are considered. In this work, only a 300 K cold utility is considered to ensure compliance with energetic self-sufficiency. The work/cold utility cost ratio is 25/1, while the downward (hot stream) and upward (cold stream) minimum approach temperatures are 5 K for each. The temperature-entropy (T-S) diagram of the heat and power integrated flowsheet is shown in **Figure 2**, in which the process requires two heat engines and two heat pumps to satisfy the energy requirements of the flowsheet.



**Figure 2. Temperature-Entropy (T-S) diagram of the Heat Engine/Pump Network**

## 6. Economic (Operating Cost) Analysis

A preliminary economic analysis is carried out on the proposed coal to formic acid and power process, as well as for an Integrated Gasification Combined Cycle, for the comparison purposes.

In the previous section, assumptions were made for the heat and power integration analysis: the abstract heat engine/pump operations are isentropic, while the specific turbine/compressor/pumping operations employed in the flowsheet feature 85% adiabatic efficiencies. Oxygen feed is assumed to be pure, but the cost of air separation is still accounted for. All other power consumption (pumps, compressors, etc.) is reflected in the flowsheet's net power generation calculations.

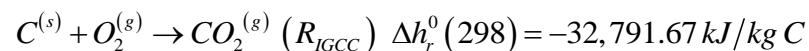
The operating cost includes coal and water purchase. The operating revenue include the sale of formic acid and power. The profit margin amounts to \$86.084/h per 0.01201 kg/s feed of coal, translating to \$2.009/s per 1 kg/s of coal feed. **Table** shows the details about operating cost analysis.

	Unit Cost	Unit	Unit Cost Ref.	Net Amount Consumed	Unit	Economic Value (\$/h)
<b>EXPENDITURE</b>						
<b>Coal</b>	0.038	(\$/kg)	[9]	0.01201	(kg/s)	1.6454
				43.3	(kg/h)	
<b>O<sub>2</sub> Production Power Consumption</b>	0.105	(\$/kWh)	[9]	24	(kW)	2.52
<b>Water Operating Cost</b>	0.441	(\$/kg)	[27]	0.01802	(kg/s)	28.6209
				64.9	(kg/h)	
<b>Total Expenditure:</b>						32.7863
<b>REVENUE</b>						
<b>Formic Acid</b>	0.7	(\$/kg)	[18]	0.04602	(kg/s)	115.99
				165.7	(kg/h)	
<b>Electricity</b>	0.105	(\$/kWh)	[9]	36	(kW)	3.78
<b>Total Revenue:</b>						119.77
<b>Profit Margin:</b>						86.9837
<b>Profit Per (kg/h) Feed of Coal:</b>						2.00886143

**Table 2. Operating cost analysis of proposed process**

Note that the flowsheet generates 60 kW electrical power and oxygen production consumes 24 kW. Thus, the net electricity production is 36 kW.

The superior profitability of the proposed process is revealing when it compared to a conventional Integrated Gasification Combined Cycle (IGCC) power plant consuming coal and generating power ( $R_{IGCC}$ ).



$$\Delta h_r^0(298) = -32,791.67 \text{ kJ/kg } C \times 0.01201 \text{ kg } C/s = 393.83 \text{ kW}$$

For this analysis, we assume that a coal power plant is operated using an ideal Carnot cycle, and then an 85% adiabatic efficiency is imposed on it. The Carnot cycle is considered to operate at temperature limits matching those of the proposed formic acid cycle. This corresponds to 1250 K and 300 K, the highest and lowest temperature of the formic cycle. The Carnot cycle efficiency within this temperature limits is 76.0%, which reduces to 64.6% when the 85% efficiency is imposed on the cycle's turbomachinery operations. When 90% carbon capture is incorporated, the relative efficiency penalty is 22% [29] and so the overall efficiency reduces to 50.4%. The amount of power generated for both zero and 90% carbon capture is shown below:

$$W_{IGCC(no\ capture)} = 0.646(393.83) = 254.41kW$$

$$W_{IGCC(90\% \ capture)} = 0.504(393.83) = 198.49kW .$$

For this ideal coal-fired power plant, the cost elements involve only the purchase of coal feed and the revenue consist of the sale of produced electricity. This amounts to \$0.579/s per 1 kg/s of coal without CO<sub>2</sub> capture and \$0.443/s per 1 kg/s of coal with a 90% CO<sub>2</sub> capture. **Table** gives a demonstration of the economic analysis.

	Unit Cost	Unit	Unit Cost Ref.	Net Amount Consumed	Unit	Economic Value (\$/h)
<b>EXPENDITURE</b>						
<b>Coal</b>	0.038	(\$/kg)	[9]	43.3	(kg/h)	1.6454
<b>Total Expenditure:</b>						1.6454
<b>REVENUE</b>						
<b>Electricity (0% Capture)</b>	0.105	(\$/kWh)	[9]	254.41	(kW)	26.71305
<b>Electricity (90% Capture)</b>	0.105	(\$/kWh)	[9]	198.49	(kW)	20.84145
<b>Profit Margin (0% Capture):</b>						25.06765
<b>Profit Margin (90% Capture):</b>						19.19605
<b>Profit Per (kg/h) Feed of Coal (0% Capture):</b>						0.57892956
<b>Profit Per (kg/h) Feed of Coal (90% Capture):</b>						0.44332679

**Table 3. Operating cost analysis of compared baseline**

The operating profit of the proposed power plant is higher by 247% when compared to a coal power plant without carbon capture. The increase reaches to 353% when ninety percent carbon capture is considered in the coal power plant baseline. In addition to superior operating cost performance, the proposed formic acid process ensures over 99.98% carbon capture

## 7. Discussion-Conclusions

In order to assuage the greenhouse effect, a novel process for the coal power plants with no carbon dioxide emissions was developed. CO<sub>2</sub> is 100% utilized to synthesize formic acid, which increases the overall process commercial profitability. At the same time, the feasibility of this proposed process is justified and the whole system is energetically self-sufficient. Heat and power integration is carried out to calculate the amount of power produced from the process while remaining energetically self-sufficient. A preliminary economic analysis reveals a 247% and 353% operating profit increase when the process is compared to a conventional coal power plant with the same amount of coal feed operated at 0% and 90% carbon capture scenarios respectively.

## 8. Nomenclature

$B_i$  - Thermodynamic availability of the  $i$ -th stream

$C_j$  - System species

$g_i$  - Specific molar entropy of material stream  $i$

$G_i$  - Specific mass Gibbs free energy of material stream  $i$

$h_i$  - Specific molar enthalpy of material stream  $i$

$H_i$  - Specific mass enthalpy of material stream  $i$

$L$  - Rate of lost work

$\dot{m}_i$  - Mass flowrate of material stream  $i$

$M_j$  - Molecular weight of the  $j$ -th species

$P_i$  - Pressure of the  $i$ -th stream

$\dot{Q}_0$  - Rate of heat escaping from the system to the surroundings

$s_i$  - Specific molar entropy of material stream  $i$

$S_i$  - Specific mass entropy of material stream  $i$

$S_C$  - Index set of components (species) present in at least one material stream

$S_E$  - Index set of constituent elements

$\dot{S}_G$  - Rate of entropy generation

$S_I$  - Index set of inlet material streams

$S_O$  - Index set of outlet material streams

$T_0$  - Reference temperature

$T_i$  - Temperature of the  $i$ -th stream



$\dot{W}_{s,j}$  - Rate of shaft work consumed by the  $j$ -th source in the system

$x_{i,j}$  - Mass fraction of  $j$ -th species in stream  $i$

$\Delta g_{f,i}^0$  - Standard state Gibbs free energy of formation of the  $i$ -th species

$\Delta \dot{G}_s(T_0)$  - Rate of Gibbs free energy change of system at reference temperature

$\Delta h_{f,i}^0$  - Standard state enthalpy of formation of the  $i$ -th species

$\Delta \dot{H}_s(T_0)$  - Rate of enthalpy change of system at reference temperature

$\Delta s_{f,i}^0$  - Standard state entropy of formation of the  $i$ -th species

$\mu_j$  - Component coefficient of stream  $j$

$\nu_{j,k}$  - Stoichiometric coefficient of element in the  $j$ -th species  $k$

$\Omega$  - Open, well delimited system or control volume

$\dot{\eta}$  - Normalized flowrate

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