**Syngas Production from Petroleum Coke Gasification**

University of Illinois

Chemical Engineering

Senior Design Project

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**Abstract**

Petroleum coke is a major byproduct that historically has been used as a substitute for coal in power production or as a fuel in cement manufacture. The decreasing quality of crude oil refined in the United States means that more petroleum coke is being produced, often with much higher metals and sulfur content. Our objective is to evaluate a better route for using low quality petroleum coke by converting it into a feed for our linked acetic acid production team while capturing all of the sulfur, metals and most of the CO2 from combustion. Since petroleum coke is linked to the refining of crude oil, it is available at much lower cost and in much larger quantities than bio-feeds. In addition, because petroleum coke is a byproduct, and not directly extracted from the environment, it lacks the negative land use impacts of bio-feeds.

In our process, petroleum coke along with oxygen and steam are fed into an entrained flow gasifier to produce synthesis gas, a combination of carbon monoxide, hydrogen, carbon dioxide and hydrogen sulfide. Sulfur is a poison to downstream chemical production catalysts and must be removed from syngas to ppm levels by the Claus process. A significant advantage of our process is that unlike burning petroleum coke for conventional power, the CO2 from combustion can be captured and sent via pipeline for sequestration, or enhanced oil recovery. Aspen, a thermodynamic simulation tool, is used to establish the material and energy balance for the overall process.

**1. Introduction**

**1.1: Petroleum Coke Background**

**1.2: Gasification Technology**

**Figure 1.2-1: Shell Gasifier System (Higman, Burgt 119)**

The ground, pressurized coke is transported along with Nitrogen gas (Because Nitrogen is an inert gas). This petcoke is supplied with 95% Oxygen and steam through nozzle of the burner on the wall. The temperature inside the reactor is about 2700 ⁰F and pressure is around 350-600 psi which speeds up the reaction. As a result, the syngas leaves the reactor from the top through the lock hopper .The steam that is left behind, leaves the reactor through the annular space at medium pressure.

The slag comes down in the reactor where it is quenched in a water bath. The Boiler Feed Water (BFW) supplied to annular wall of the gasifier is used as water bath. The huge temperature drop due to water bath results into hardening of the slag. This slag is ground by slag crusher. The granulated slag leaves the reactor through the lock hopper and the Boiler Feed Water (BFW) supplied to cool the slag, moves to heat exchanger. The BFW water is supplied that liquefies the slag.

The syngas goes into the heat exchanger where it’s cooled by supplied Boiler Feed Water (BFW). As a result, syngas moves down the heat exchanger and water leaves the heat exchanger as High Pressure Steam. Additional Boiler Feed Water (BFW) is supplied from the bottom nozzle of the heat exchanger that cools the syngas even more. This water comes out of the heat exchanger as medium pressure and the syngas leaves the heat exchanger at approximately 536⁰F and passes a candle filter unit where the solids from the gas are removed. About half the gas is then recycled via recycle gas compressor as quench gas and the other half is cooled in water scrubbing system.

|  |  |
| --- | --- |
| Syngas Quench (Maurstad 26) | |
| At the outlet of the gasifier reactor the temperature of the syngas is around 1500°C and the fly ash (or slag) is in liquid form. To protect downstream process equipment from fouling, a quench is needed to solidify the slag and make it non-sticky. | |
| Water Quench   * A water quench uses sensible heat from the syngas to vaporize water. * The quench may be total as in the simplest version of the GE gasifier where the syngas is saturated with water vapor, or it may be partial where the syngas is only cooled down to around 900°C. * In the latter case, heat recovery by production of HP steam would be included. * In both cases, the addition of water drives the water gas shift reaction to increase the H2/CO ratio which is beneficial in the case of CO2 capture. |  |
| Radiant Syngas Cooler   * The radiant syngas cooler is available in one version of the GE gasifier. * The hot gas flows into a radiant boiler where saturated steam is generated. * At the Tampa IGCC demonstration plant, problems with the seals protecting the cooler shell from hot syngas caused five forced outages from 1997 to 2001, but the operators felt a solution was close |  |
| Quenching by Recycle   * Quenching by recycle of cooled syngas is applied in the Shell gasifier. * After particle removal in the candle filter, about half of the syngas flow which has a temperature around 300°C is recompressed and recycled to the gasifier outlet. * By mixing the 1500°C hot syngas with the recycle stream, a cooling down to around 900°C is achieved. * Heat is then recovered in a convective syngas cooler. | N/A |
| Chemical Quench   * Chemical quench is a concept which has less experience, but offers some interesting advantages. * The principle is the addition of a second gasification step which uses the sensible heat in the hot syngas, and not oxygen, to gasify the coal feed with water. * This ensures that the second stage is non-slagging (slag is solid). Because the outlet gas temperature is decreased and has less sensible heat, the cold gas efficiency is increased. * A disadvantage is that some tars, which make gas cleanup more complex, may be formed. Conoco Philips’s slurry feed gasifier (E-gas) incorporates this principle. | N/A |

References:

Higman, Chris, and Maarten Van Der. Burgt. *Gasification*. Amsterdam: Gulf Professional Pub./Elsevier Science, 2008. Print.

Maurstad, Ola. *An Overview of Coal Based Integrated Gasification Combined Cycle (IGCC) Technology*. Rep. Cambridge: Massachusetts Institute of Technology, 2005. *For Energy and Environment*. Scribd. Web. 2 Feb. 2011. <http://www.scribd.com/doc/35269273/24/Syngas-quenching>.

**2.4: Water Gas Shift Reactors**

A water as shift reaction is a reversible exothermic reaction where the reactants are carbon monoxide and steam and the desired products are hydrogen gas and carbon dioxide. The reaction is show below.

COH2O CO2 H2 (-39.01BTU/mol)

The reason this reaction process is necessary in the process is because the syngas must be at a 2: 1 molar ratio of H2: CO. The feed stock petcoke has a large carbon content and therefore mainly produces CO and CO2 with very little H2 being produced in comparison. Since such a large amount of CO is produced the syngas stream will be split and one part will remain with its high concentration of CO while the other is feed into water gas shift reactors to convert the CO to H2. The two streams will be combined in order to produce the desired molar ratio.

The kinetic of the reaction are important in order to determine the amount of desired products produced. The two main variables in the kinetic are temperature and pressure. The pressure does not affect the reaction significantly since both sides contain the same moles of gas. The equilibrium constant (products over reactants) is highly affected by temperature and can be shown by the graph below.



**Figure 2.4-1: Shows equilibrium relation to temperature (# reference)**

The equilibrium constant is also calculated with the empirical equation shown below.



The graph and equations show a favorable leaning toward low temperature reaction settings.

Water gas shifts are typically conducted in two stages an initial high temperature shift (HTS) then followed by a low temperature shift (LTS). Both of these reactors contain a certain amount of catalyst in relation to the feed amount. There are a variety of catalyst technologies that cater to specific shifting requirements. The following are a few of the catalyst bases available, Ferrochrome, Copper-Zinc and Cobalt – Molybdenum.

**2.5: Hydrogen Sulfide and CO2 Removal Process**

After the syngas has had any particulates removed it is then sent to the section of the plant to remove H2S and CO2. This is a pretty lengthy processes involving multiple absorbers and stripping columns to ensure that the final syngas is primarily H2 and CO­2. The most important component in this system is the absorption solvent, Selexol, which is physical solvent. Which means it does not react with the components it is removing as compared to a chemical solvent, like the commonly used MDEA. Selexol is a mixture of dimethyl ethers of polyethylene glycol with the empirical formula of CH3(CH2CH­2O)nCH3 where n is between 3 and 91. Another key difference between chemical and physical solvents is their relationship with partial pressure and their solvent loading capacity. Chemical solvents tend to plateau off at higher partial pressures unlike chemical solvents which just increase linearly with increasing partial pressure1. In the case of our system it is necessary to use a physical solvent such as Selexol to ensure that the final syngas has as little sulfur as possible and also because our process is on such a large scale where the partial pressure will be factor in the overall loading capacity. Selexol will also insure that our acid gas to the Claus plant is greater than 45% H2S, which is necessary for the Claus process to perform properly.

The process begins by sending the cooled, particulate freed syngas to the H2S absorption column where the gas is contacted with already pre-loaded Selexol which is from the CO2 absorber. The solvent is pre-loaded with CO2 ­to ensure that the CO­2 ­in the incoming gas is not absorbed on the Selexol which minimizes the temperature rise across the column1. The H­2S rich solvent then is removed through the bottom of the absorption column and sent to the regeneration cycle while the syngas and CO2 exits through the top of the absorber and is sent to the CO2 absorption process.



**Figure 2.5-1: H2S Absorption Column1**

The H2S rich solvent is then sent through a rich/lean solvent heat exchanger where the rich solvent is heated and the lean is cooled. The H2S rich solvent is then sent to a concentrator which runs at a greater temperature than the H2S absorber to remove the CO­2 to be recycled back into the feed stream for the H2S absorber1. The concentrated H2S rich solvent is then flashed to a lower pressure where the flash gas contains a higher proportion of CO2 which is then recompressed and sent back to the feed of the H2S absorber. The concentrated H2­S rich solvent then leaves the flash and is sent to the top of the H­2S stripping column where the solvent will be regenerated. The stripper removes the H2S from the Selexol where it exits through the top of the column as acid gas containing >45% H2S which will then be used in the Claus plant deal with the sulfur1. The now lean solvent leaves the stripper through the bottom and is sent to same rich/lean solvent exchanger as before where it is cooled and then cooled even more by NH3 refrigeration.



**Figure 2.5-2: H2S Regeneration Process1**

This lean solvent is then fed into the top of the CO2 absorption column where it removes the CO2 from the partially treated gas from the H2S absorber. The final syngas then exits the top of this absorber and is almost ready for use in chemical production. CO2 rich solvent comes out of the bottom where the stream is split so some is sent to the H2S absorber as the CO2 ­saturated solvent feed and the other is sent to the CO2 solvent regeneration.



**Figure 2.5-3: CO2 Absorption Column1**

This CO2 solvent regeneration is comprised of three flash vessels. The first flash vessel is the same pressure as the one used in the H2S regeneration step so that only one compressor is required that could handle the loads of both streams1. The other objective of this first flash is to recover and H2 that has been absorbed in the Selexol. The second flash takes off most of the CO2 where it is then sent to the purification process to make an end product that is 99% pure CO21. The final flash sends any remaining CO2 to the atmosphere and then sends the semi-lean solvent back to be used in the CO2 absorber.



**Figure 2.5-4: CO2 Flash Regeneration1**

The final step in this cleaning process is CO2­ purification. The raw CO2 feed gas is sent over a zinc oxide catalyst where any COS present is converted to H2S and then absorbed onto the ZnO catalyst. These reactions are the following:

COS + H2O 🡪 CO2 + H­2S

H2S + ZnO 🡪 ZnS + H2O

The gas leaving the ZnO bed is then sent over a platinum oxidation catalyst where the following reactions take place:

CO + ½ O2 🡪 CO2

H2 + ½ O2 🡪 H2O

CH4 + 2 O­2 🡪 CO2 + 2 H2O

This then leaves the remaining gas with 99% pure CO2 to be used where ever seems necessary.



**Figure 2.5-5: CO2 Purification1**

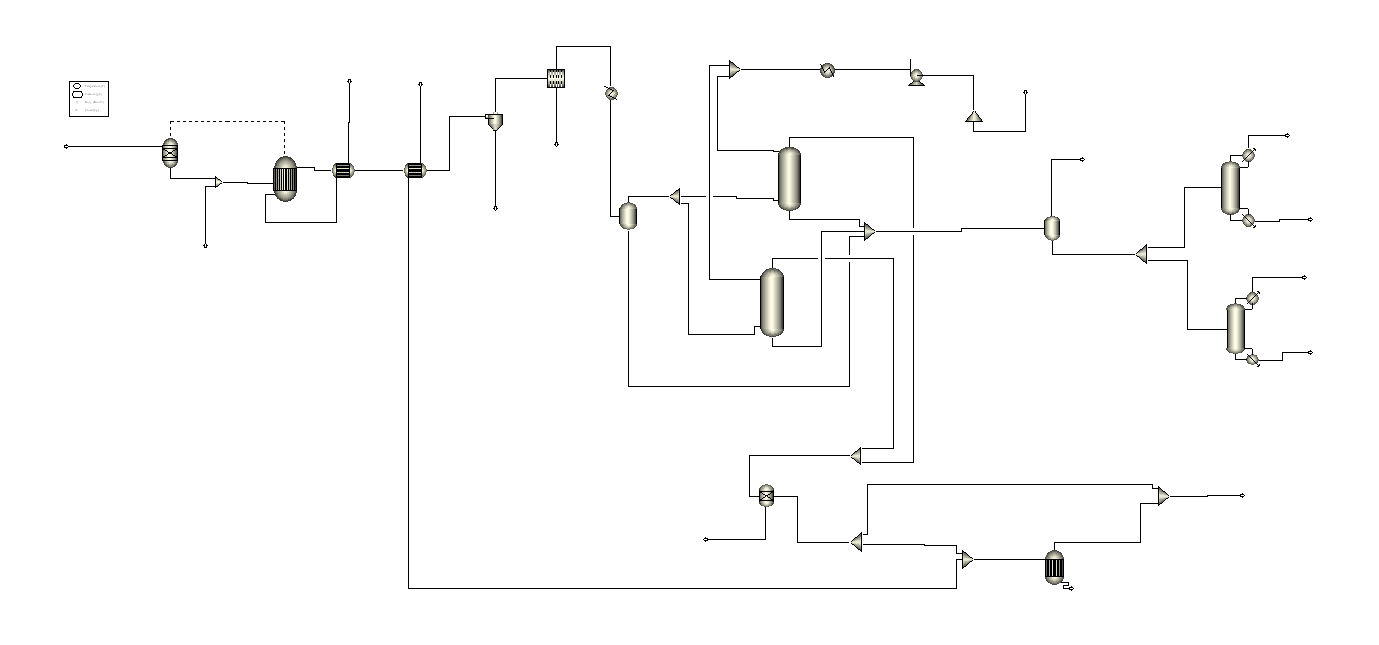
References:

(1) Breckenridg, William, Allan Holiday, James O Y Ong, and Chris Sharp. *Use of SELEXOL Process in Coke Gasification to Ammonia Project*. *Use of SELEXOL Process in Coke Gasification to Ammonia Project*. 1 Mar. 2000. Web. <http://www.uop.com/objects/92SelexCokeGasifAmm.pdf>.

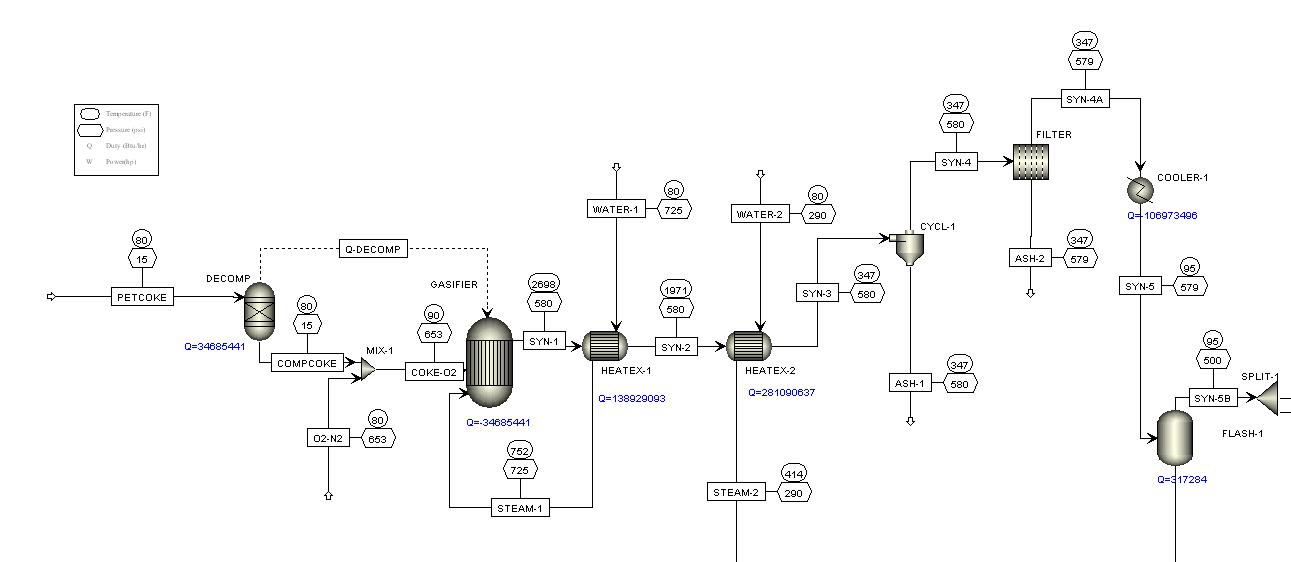
**2.6 Claus Process**

**Figure 2.6-1: Claus Process**

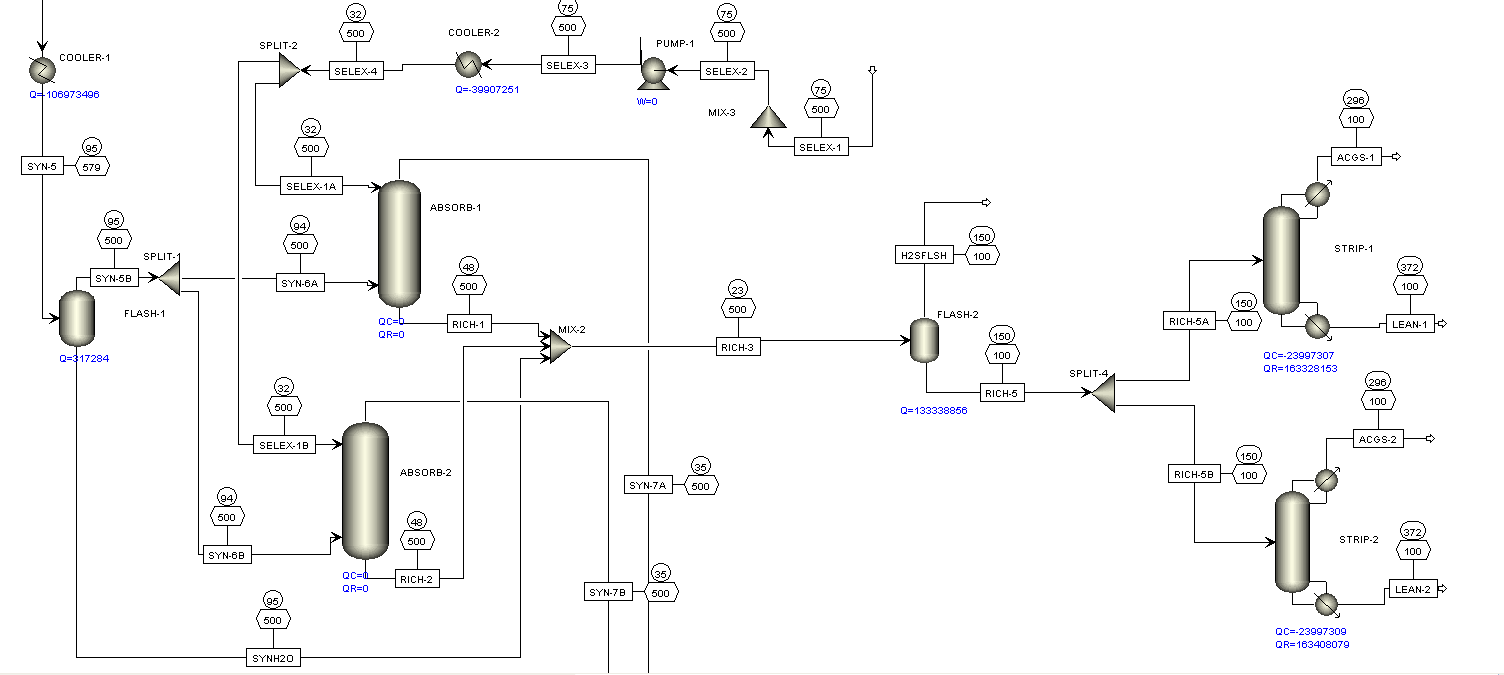
**3. Aspen Plus Simulation**



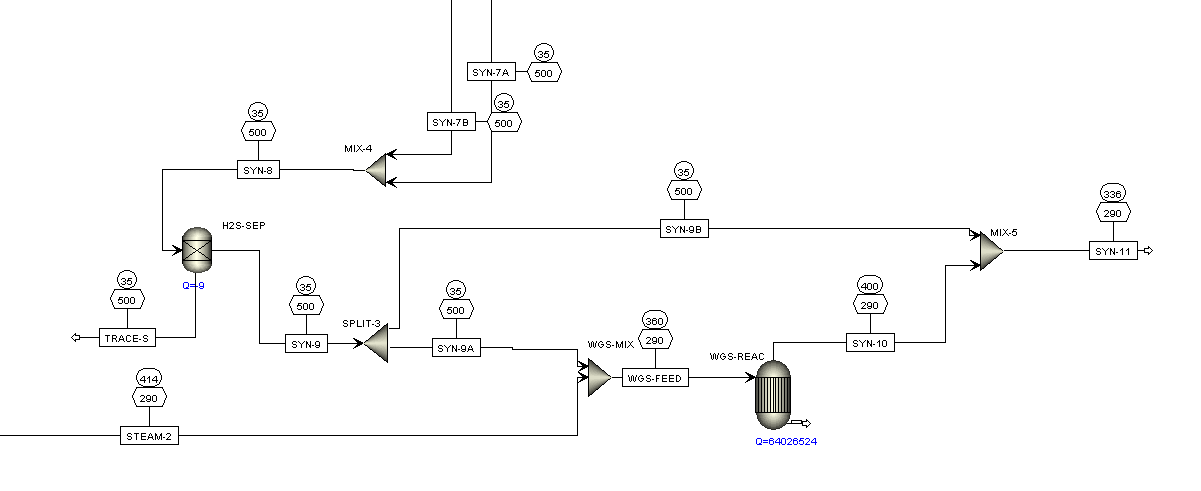
Overall process (not including the Claus process, CO2 recovery and petcoke crushing and ASU unit if necessary)



This is the Gasification section, its stops after Cooler-1. From there it goes to the H2S Scrubbing section. Top number attached to stream is temp(F) and bottom is pressure (psi) the blue is heat duty.



This is the H2S scrubbing along with the solvent (Selexol) regeneration columns. The two main parts are the exiting clean syn gas going to the WGS and the Acid gas leaving the strippers. NOTE: The lean solvent has to be recycled back to the absorbers by meeting up with Mix-3 that is not shown yet because of convergence issues.



This is the WGS section. We don’t need a rigorous modeling of this because this isn’t a power plant where we have to make as much H2 as possible.

**Screenshots of Aspen Plus Data (Mass)**

















**Screenshots Aspen Plus Data (Mole)**

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**APPENDIX A. Design Basis**

The objective of our process is to design a gasification system to produce synthesis gas for a downstream acetic acid production team (Team Golf). We have decided to use petroleum coke as our feedstock in this process since petroleum coke, petcoke, is high in carbon content and cheaper price. However it does have its drawbacks as well, primarily its high sulfur content. This creates a challenge when trying to remove the sulfur, due to its poisonous effects on downstream catalysts, to ppm levels in the final synthesis gas.

It has been specified that they need 3000 tons per day of syngas with a CO:H2 mole ratio of 0.40 and a C:H mole ratio of 0.23.

**APPENDIX B. Block Flow Diagrams**



**Figure A-1: Simplified Block Flow (With Tons/day)**



**Figure A-2: Block Flow (With Stream Numbers)**



**Table A-1: Component Material Balance for Figure A-2**



**Table A-2: Element Balance for Figure A-2**



**Figure A-3: Overall Block Flow Diagram**