Urea Manufacture by Novel Techniques Utilizing Alternate Raw Material Sources

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A sustainable process for urea production, (named Sust-E or sustainably engineered urea process) has been proposed utilizing Aluminum, Steam and Industrial Flu-gas as raw materials as opposed to Natural Gas, Air and Steam used in existing processes. It is sought to achieve mass-scale production while reducing burden on fossil fuel reserves through a sustainable, cleaner and cheaper process. The Aluminum-steam reaction is explored as hydrogen source for ammonia synthesis - an intermediate step in the process. This reaction has been presented in literature for various vehicular, hydrogen and power generation applications; however, industrial scale urea production through this method has not been studied.

Application of membrane processes is investigated for flu gas separation to provide nitrogen and carbon dioxide for ammonia and urea synthesis, respectively.

Economic feasibility of the process is evaluated by designing a 7000 tpd urea plant and verified by simulation in Aspen Plus.

A number of novel techniques are integrated into one sustainable process which replaces the front-end of the ammonia plant while the remaining plant is unchanged.

Aluminum is an excellent energy carrier, with energy per unit volume following those of Boron and Beryllium. [Golovitchev, 2011]. It stores this energy during its manufacturing process. Aluminum is manufactured by electrolysis in the Hall-Heroult process which is very energy intensive and results in carbon dioxide emissions. The establishment of Sust-E Urea Plants will generate a greater demand for Aluminum requiring the Aluminum industry to expand. However, non-consumable cathodes are being developed for this process which would tremendously reduce carbon dioxide emissions. [Lorentsen, 2000] The energy requirements of the aluminum manufacturing process can be fulfilled using renewable energy. It is proposed to use concentrated solar power (CSP) technology to fulfill the energy requirements of both the Sust-E Urea Plant as well as the Aluminum industry that would be established.

The first part of the new front-end is the Aluminum-steam reactor which produces hydrogen for ammonia production by the Haber-Bosch process. The Aluminum-steam reaction is a highly exothermic reaction favorable at all temperature and pressure conditions. [Petrovic, 2010] However, kinetics is slow with respect to industrial applications under ambient conditions. Once ignited at higher temperatures, the reaction occurs explosively fast. The aluminum particles react in the gaseous phase. [Beckstead, 2005] A combustion reaction occurs with spherical flames around particles. The flame temperature is higher than the melting temperature of the alumina product which would otherwise form a layer. [Foote, 2000]

Based on earlier work by J. P. Foote, et al. a reactor design has been selected which combusts 5 g/s of Aluminum in an atmospheric dump combustor along with steam at 150 psig and at 600 ^{o} F, having

a diameter of 4 inches and length of 48 inches. It is lined with 3 inches of refractory. Propane combustion provides ignition at start-up, but later the heat of aluminum steam reaction is enough to sustain the reaction. The aluminum is ignited 18 inches downstream the inlet and reaction is completed about 24 inches further downstream. In within 60 ms of total residence time the combustion is completed with about 95% efficiency. In this experiment a particle size of 17 μm has been used. [Foote, 2000]

The same conditions will be used in the Sust-E plant, so as to ensure reliability of the results. Under these conditions, the favorable reaction is $2\ Al + 3\ H_2O \rightarrow Al_2O_3 + 3H_2$. This reaction has the advantage of having a higher yield of hydrogen with respect to water, compared to reactions taking place at lower temperatures, which produce hydroxides of Aluminum. [Petrovic, 2010]

Hydrogen will be separated from the solid product using a cyclone separator, followed by separation of unreacted steam through condensation followed by phase separations. The recovered water can then be recycled back to the boiler.

Aluminum activation is necessary before introduction into the reactor as it is passivated by a layer of aluminum oxide preventing further oxidation of the bulk Aluminum. The method chosen is that described in Watanabe's work. [Watanabe, 2004] An aluminum ingot will be ground using a Silicon Carbide tool under water exposing fresh unreacted Aluminum sites for reaction. Particle sizes as low as 20μm are produced by this tool. It is assumed that the reaction of the 20 μm particle will be similar to the reaction of the 17μm particles. Therefore, 20 μm aluminum particles will be used in the reaction. It is proposed to use the same water to fluidize the aluminum particles for ease of conveying.

15442 tubes will be connected to the steam header. They will be stacked such that there are about 16 stacks of 34 rows having 29 tubes each. The reason for having a number of small tubes is to ensure ample heat transfer surface to provide same heat loss as the laboratory conditions. If sufficient heat is not lost, the heat of reaction would cause high temperatures, faster kinetics releasing in greater heat generation and hence, a runaway reaction.

At start-up propane will be combusted to heat up the reactor and its products will be vented. Once the reactor is heated up, steam will be introduced followed by closing of the vent and introduction of Aluminum.

The product of the tubes which is at about 2900 K will be combined in a refractory lined header and proceed to the boiler for heat recovery as steam. High pressure steam will be produced by the boiler and used to drive a turbine. Steam at 150 psig and 600 ^{o} F will be extracted from the turbine to supply feed to the reactor. However, at start-up a secondary boiler will be required to supply steam.

The heat of reaction will provide roughly 1100 MW of energy of which 405 MW would be lost to the surroundings, while 280 MW will be used to provide steam for feed, the remaining can be recovered as electrical power and the rest utilized downstream.

It is to be noted that the Alumina produced in this reaction would only have 3% unreacted

Aluminum particles as impurity which are significantly larger than the alumina product particle and be easily separated by a filter or strainer, resulting in a high purity and high cost bi-product. The two bi-products i.e. electricity and alumina add to the feasibility of the process.

The pressure requirements for the ammonia reactor are up to 20 MPa. [Appl, 1999] The energy remaining in the hydrogen stream after heat recovery will be utilized when cold, low pressure nitrogen is mixed into it before condensation of steam. This will reduce temperature and pressure of the combined synthesis gas stream reducing the load on the condenser and separator as well as pre-heaters and compressors for synthesis gas. This also reduces safety hazards associated with pure hydrogen. The steam condensed will be separated and recycled while the synthesis gas proceeds to the backend.

The second part is flu gas separation. Flu gas is obtained from a power plant, cement factory, etc. preferably a coal fired source which is richer in carbon dioxide. After removal of ash, sulfur oxides and nitrogen oxides, this is passed through a facilitated poly vinyl amine (PVAm) membrane. As shown by Hussain's work, the permeate consists of pure CO_2 with very small quantities of nitrogen and oxygen. [Hussain. A, 2009] Nitrogen is inert and can be vented out by purging. Oxygen may be removed using carbon molecular sieve membranes.

The retentate provides nitrogen for the synthesis gas. However, it contains water vapor, oxygen and a small quantity of carbon dioxide. The water vapor will subsequently be removed in the condenser which recovers recycle water. However, carbon dioxide and oxygen would pass through and proceed to the ammonia reactor, and poison the Iron catalyst. Besides that, carbon dioxide could form an ammonium carbamate precipitate with ammonia in the recycle streams at the back-end, choking the lines. Therefore, it is essential to remove them.

A series of carbon molecular sieves is proposed, which has proved to be able to produce nitrogen of 99% purity. It adsorbs both oxygen and carbon dioxide. [Campo, 2010] Any remaining traces can be converted in the methanator. This will produce methane gas at the expense of a small quantity of hydrogen gas. Methane is inert at the back-end, and removed by purging. Purge gas is then utilized as fuel.

The Sust-E Urea process has the potential for reducing the cost of urea production. It eliminates all the steps of carbon monoxide conversion to carbon dioxide and replaces the absorption step with membrane separation. A regular cost of replacing expensive catalysts (Nickel-based, Iron-based and Copper-based) will be eliminated. The Sust-E Urea process can be incorporated into existing plants and is therefore, a very promising technology, and is worth undergoing the higher stages of process development.

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