Final Scientific Technical Report

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Ammonia Process by Pressure Swing Adsorption

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Executive Summary

The overall objective of the project is for SmartKoncept Technology, (SmartKoncept Inc), and the University of South Carolina to design, develop and demonstrate a technically feasible and commercially viable system to produce ammonia along with recovery of the products by adsorption¹⁻⁴ separation methods and significantly decrease the energy requirement in ammonia production. This is achieved through a significantly more efficient ammonia psa recovery system. The proposed method represents a major transformational technology development with potential to substantially generate large energy-saving benefits, reduce the energy consumptions, raw material usage, capital costs, and environmental burdens, while enhancing safety of industrial production of ammonia in the entire chemical industry. The proposed technology can be applied to both green plant processes as well as to retrofit and revamp existing ammonia plants in the U.S. to enable more efficient use of energy in ammonia production industry.

Ammonia, (NH₃), is widely used in the industry for a variety of purposes. More than 2,000 facilities manufacture or process ammonia in the United States. Ammonia use includes for fertilizer production, chemicals synthesis, fibers & plastics, pharmaceutical drugs, mining & metallurgy, industrial and household cleaning agents, as refrigerant in industrial facilities such as: meat, poultry, fish processing, dairy, ice cream plants, breweries, soft drink processing, cold storage warehouses. At least 225 of the 275 electric utilities and power plants in the USA use ammonia to suppress NO_x formation & remove CO₂. Ammonia production⁶⁻⁹ is a highly energy intensive process. Ammonia production is ranked 2nd (only after ethylene) as the top most energy intensive processes among all the US industries. Ammonia production consumes a total energy of 750 Trillion BTU, (equivalent to more than 129million barrels of crude oil), or more than 10% of total energy in production of top 50 major chemicals). This new innovative technology project will significantly lower the energy consumption, while also improving production efficiency.

This project has been focused on the development of a more energy efficient ammonia recovery section. The new ammonia recovery system receives the reactor effluents and achieves complete ammonia recovery, (which completely eliminates the energy intensive refrigeration and condensation system currently used in ammonia production). It also recovers the unused reactants and recycles them back to the reactor, free of potential reactor contaminants, and without the need for re-compression and re-heat of recycle stream thereby further saving more energy. The result is a significantly lower energy consumption, along with capital cost savings.

The following key goals were developed to achieve this objective:

- Perform proof of concept with bench scale experiments to gather initial equilibrium and kinetic data for the ammonia recovery sections;
- Investigate and determine process conditions which support recovery of ammonia (without the need for refrigeration compressor work requirements). Determine adsorbents that are most suitable along with their performance, stability, life span for the operating conditions;
- Design the ammonia recovery system by pressure swing adsorption;
- Design, build, and test bench scale or pilot scale unit for the ammonia recovery system that demonstrate the performance needed for a commercial process.
- Perform economic analysis and compare the expected capital and operating costs of the ammonia process to conventional processes, to show attractiveness to the end user and discuss potential transfer of technology to end users.

The project for the development of the enhanced ammonia recovery system was divided into 4-phases. Each phase had its own set milestones and tasks

Phase I: “the proof of concept phase” involved initial identification, screening and testing of new materials through laboratory experiments.

Phase II: In-depth computer simulation along with experimental tests and analysis on the materials to determine their potential performance and stability, and to enable final choice or selection of suitable materials for the ammonia recovery section.

Phase III: Construction of the full scale new ammonia recovery system, for further studies, experimental data gathering, process optimization and validation of the ammonia PSA recovery process project.

Phase IV: Final experimental data validation, scale-up design of the full system, along with Costing and analysis.

The summary of key tasks for each phase are as follows:

The key task (“Go or No Go” decision point) for Phase I, of the project was to find a potentially suitable adsorbent that would enable separation of ammonia from the synthesis reactor effluent. This has been successfully achieved. The following were successfully achieved in phase 1: i) identified suitable adsorbent for ammonia recovery ii) collected the equilibrium isotherm data from bench scale experiments iii) developed the PSA process mechanism and cycle steps conditions iv) established the optimum conditions for ammonia recovery by PSA v) established the proof of concept that PSA methods for ammonia recovery will save energy. The results from the proof of concept stage were used to guide the setup of bench scale PSA experiments in the next phase. It also provided the basis and reference for experimental validation during the second phase of this project.

The key task, (the “Phase 2 Go or No Go” decision point) for this Phase of the project was to perform in-depth bench scale experiments and analysis on adsorbent(s) with good performance, capacity, and stability of the adsorbent at the high temperature and pressure conditions. This is critical to enable final choice or selection of suitable adsorbent(s) for the ammonia PSA recovery section. Finding a suitable adsorbent is critical. Another important task is the application of simulation results to guide the construction of the full scale ammonia PSA recovery system. The construction of such a complete and functional system for ammonia recovery is important to enable successful commencement of further studies, experimental data gathering and process optimization for the prototype design and scale up (planned for phase 3) of the project. Without a suitable adsorbent, it would be very difficult to recover ammonia by PSA method and the project would become infeasible. In addition, the design and construction of a fully functional PSA system for ammonia recovery would not be possible. Furthermore, without a constructed PSA system it would also become impossible to gather more data and validate simulation results for use prototype design and scale up design to industrial level in the following phases. Project would not be feasible. This key task was successfully achieved in phase 2. A suitable adsorbent with high capacity and stability at the elevated pressure and temperature conditions was found.

The key task, (the “Phase 3 Go or No Go” decision point), for this phase of the project was to successfully test the bench scale ammonia recovery PSA unit and to demonstrate that a high purity and high recovery of NH_3 and H_2/N_2 products are achievable. The economics from the integrated flowsheet compared to conventional is also very important. This “Go or No Go” decision point is critical for two reasons: Firstly, a stable and successful operation of the ammonia PSA recovery unit is required to conduct further studies, experimental data gathering and process optimization for the prototype design and scale up of the project. Secondly, the ability to produce high purity and recovery of NH_3 and H_2/N_2 products with the PSA unit is needed as a conclusive demonstration that the new technology can be reliably adopted for the recovery of ammonia from the reactor effluent in the production of ammonia. A strong argument could then be made in the industry for the complete elimination of the energy intensive refrigeration system, currently used in

conventional methods of ammonia production and replace them with the more efficient PSA system in both retrofit and green/grass root ammonia plant designs. This task was successfully achieved. The constructed prototypes were successfully operated and high purity and high recovery of NH_3 and H_2/N_2 products achieved.

It would also be difficult to gather relevant data for process optimization studies, validation and scale-up, sizing and design for Phase 4.

The phase 4 focused on final experimental data validation, scale-up design of the full system, along with costing and economic analysis. This was successfully completed. The new method was confirmed to be more efficient, with significant energy savings than existing methods.

Potential Impact and Benefits of the New Project: The economic benefits of the proposed technology show a potential saving or reduction of more than 40% in the energy with the proposed new method. The energy savings and capital cost reduction result from elimination of refrigeration system, compression/recompression; and reduction in number of process units & sizes. Other Benefits include:

- potential 40-50% reduction in energy consumption, with high return on investment.
- new adsorbents observed to be very stable at elevated temperature and pressure conditions. They showed no signs of adsorbent deterioration, and suffered no irreversibility or physical structural
- high purity and recovery of ammonia, with NH_3 purity of 99.56 % and NH_3 recovery of 99.72 % achieved. This purity and recovery is much better compared to conventional methods.

What remains to be done: The design, construction and demonstration of a new prototype technology for efficient recovery and production of ammonia was successfully achieved. However, a new enhanced reactor system needs to be developed, tested and validated, and demonstrated in a pilot scale level. In addition, both the proposed ammonia synthesis reactor and the new ammonia psa separation recovery system, (by adsorption), need to be integrated to work together, to realize the huge potential energy saving benefits offered by the new technology. The integrated system would need to be tested, validated, and demonstrated together in order to fully convince potential end users of the viability of the new technology for ammonia production. More funding would thus be required to complete the project.

We envision a 3-year plan, for the project during which we would carry out the development, testing, validation and demonstration of the enhanced reactor and the integrated ammonia reactor and separation recovery system. During Year 1, we will build, test and validate the pilot-scale of the new enhanced ammonia synthesis reactor system designed during the concept definition stage. In Year 2, we will integrate the enhanced reactor system with the ammonia psa recovery system. We will demonstrate the integrated units working together as one single integrated pilot-scale unit. We will operate the integrated pilot scale and gather data for verification. In year 3, we will operate the integrated system further and complete testing, verification and validation. We will also perform the final engineering analysis and verification, optimization of operating conditions, scale up design and detailed comparative economic analysis for the energy, capital and operating costs of the ammonia process, to show attractiveness of the new technology to potential end users. We will discuss the potential transfer of technology to end users in the ammonia industry.

Acknowledgment and Disclaimer

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Disclaimer: “Any findings, opinions, and conclusions or recommendations expressed in this report are those of the author(s) and do not necessarily reflect the views of the Department of Energy.”

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1. Introduction

Integrated Ammonia Reactor and Ammonia PSA Recovery

The overall objective of this project is to design, develop and demonstrate a breakthrough process for energy efficient production of ammonia based on the highly integrated reaction and adsorption separation technology.

Ammonia, (NH_3), is widely used in the industry for a variety of purposes including Power plants (at least 225 of the 275 electric utilities and power plants in the USA); Fertilizer production (including ammonium sulfate, ammonium phosphate, ammonium nitrate); Chemicals synthesis (such as nitric acid, sodium hydrogen carbonate, hydrogen cyanide, as well as hydrazine), Fibers & Plastics (such as nylon), Pharmaceutical drugs (such as sulfonamide), Mining & Metallurgy, and in industrial and household cleaning agents. Ammonia is widely used as refrigerant in industrial facilities such as: meat, poultry, and fish processing facilities, dairy and ice cream plants, wineries and breweries, fruit juice, vegetable juice, and soft drink processing facilities, cold storage warehouses, other food processing facilities, seafood processing facilities aboard ships, and petrochemical facilities.

Recent DOE-EERE-ITP studies have consistently ranked ethylene and ammonia as the top two most energy intensive processes among all the US industries. Ammonia production consumes a total energy of 750 Trillion BTU, (equivalent to more than 129 million barrels of crude oil), or more than 10% of total energy in production of top 50 major chemicals). Many of ammonia derivatives are also ranked among the top 50 (including nitric acid, ammonium nitrate, ammonium sulphate and urea).

New innovative methods are needed to address and improve (the chemistry and separation methods of) older processes that are not energy efficient. This project focuses on development of a more energy efficient way to produce ammonia. It aligns well with the U.S. chemical industry's need.

The Rising Energy Cost: Cost of Natural Gas / Energy.

Natural gas is a key component for the production of Ammonia. It is used in two forms: i) to produce or provide the hydrogen which is combined with Nitrogen in the synthesis reactor to produce the ammonia; ii) as an energy source to produce energy to heat the reformers and to generate utilities during ammonia production in other parts of the process.

The price of natural gas has increased substantially over the years. This rapid price rise further underlines the need to develop more energy efficient processes. The price of natural gas peaked at about \$16 per 1000 cubic feet at end of 2008, and has now fallen to around 50% of that value by the end of 2010. However, the price forecast to start rising again from 2011, exceeding the previous historic peak afterwards..

Graph 2: Historic Average Price 1990 – 2010

As could be seen from these price trends, reducing energy consumption in ammonia production is critical. The proposed new method is expected to reduce natural gas consumption by more than one-third. This will represent a huge reduction in energy cost.

Potential Impact and Benefits of the New Project: The economic benefits of the proposed technology show a potential saving or reduction of more than 40% in the energy with the proposed new method. The energy savings and capital cost reduction result from elimination of refrigeration system, compression/recompression; and reduction in number of process units & sizes. Other Benefits include:

- potential 40-50% reduction in energy consumption, with high return on investment.
- new adsorbents observed to be very stable at elevated temperature and pressure conditions. They showed no signs of adsorbent deterioration, and suffered no irreversibility or physical structural
- high purity and recovery of ammonia, with NH_3 purity of 99.56 % and NH_3 recovery of 99.72 % achieved. This purity and recovery is much better compared to conventional methods.

Who will Use the New Technology – the Target Market

(a): Ammonia Manufacturing Plants: There are 2,338 facilities that manufacture or process ammonia in the United States. The amount manufactured or processed range from small amount (less than 100,000 pounds) to very large amount (upto 500 million pound). The proposed new technology is scalable and can be easily adopted by these ammonia production facilities in the USA.

(b): Electric Utility and Power Generation Plants: At least 225 of the 275 US electric utility and power plants in the USA use ammonia to suppress NO_x formation & remove CO_2 from flue gas in the burners. All of these power generation plants will also benefit from adopting this new technology for direct on-site production of ammonia “on-demand or on need”. Through the new technology, small ammonia production units can be integrated and used directly where and when needed, thus eliminating the current practice of hazardous transportation, on-site storage and simplifies supply logistic, and safety is improved.

What remains to be done: The design, construction and demonstration of a new prototype technology for efficient recovery and production of ammonia was successfully achieved. However, a new enhanced reactor system needs to be developed, tested and validated, and demonstrated in a pilot scale level. In addition, both the proposed ammonia synthesis reactor and the new ammonia psa separation recovery system, (by adsorption), need to be integrated to work together, to realize the huge potential energy saving benefits offered by the new technology. The integrated system would need to be tested, validated, and demonstrated together in order to fully convince potential end users of the viability of the new technology for ammonia production. More funding would thus be required to complete the project.

We envision a 3-year plan, for the project during which we would carry out the development, testing, validation and demonstration of the enhanced reactor and the integrated ammonia reactor and separation recovery system. During Year 1, we will build, test and validate the pilot-scale of the new enhanced ammonia synthesis reactor system designed during the concept definition stage. In Year 2, we will integrate the enhanced reactor system with the ammonia psa recovery system. We will demonstrate the integrated units working together as one single integrated pilot-scale unit. We will operate the integrated pilot scale and gather data for verification. In year 3, we will operate the integrated system further and complete testing, verification and validation. We will also perform the final engineering analysis and verification, optimization of operating conditions, scale up design and detailed comparative economic analysis for the energy, capital and operating costs of the ammonia process, to show attractiveness of the new technology to potential end users. We will discuss the potential transfer of technology to end users in the ammonia industry.

2. Project Objectives

The overall objective of the project was to design, develop and demonstrate a technically feasible and commercially viable system to produce ammonia along with recovery of the products by adsorption separation methods and significantly decrease the energy requirement in ammonia production.

The following key goals were developed to achieve this objective:

- Perform proof of concept with bench scale experiments to gather initial equilibrium and kinetic data for the ammonia recovery sections
- Investigate and determine process conditions which support recovery of ammonia (without the need for refrigeration compressor work requirements). Determine adsorbents that are most suitable along with their performance, stability, life span for the operating conditions
- Design the ammonia recovery system by pressure swing adsorption
- Design, build, and test bench scale or pilot scale unit that demonstrate the performance needed for a commercial process.
- Perform economic analysis and compare the expected capital and operating costs of the ammonia process to conventional processes, to show attractiveness to the end user and discuss potential transfer of technology to end users.

The method investigated represents a major technological advance with potential to substantially reduce the energy consumptions, raw material usage, capital costs, and environmental burdens, while enhancing safety of industrial production of ammonia in the entire chemical industry. Furthermore, the method could be applied to both green fields process as well as to retrofit and revamp existing ammonia plants in the U.S. The new approach for ammonia production offers key technological innovations and benefits.

3. Project Implementation Strategy

The project was divided into 4-phases. Each phase had set milestones.

Phase I, “the proof of concept phase” involved initial identification, screening and testing of new materials through laboratory experiments.

Phase II of the project involved indepth computer simulation along with experimental tests and analysis on the materials to determine their potential performance and stability, and to enable final choice or selection of suitable materials for the ammonia recovery section.

Phase III of the project involved construction of the full scale new ammonia recovery system, for further studies, experimental data gathering, process optimization and validation of the ammonia psa recovery process project.

Phase IV of the project involved final experimental data validation, scale-up design of the full system, along with Costing and analysis.

This report summaries the key findings and conclusions, as obtained in the Final Phase of the project.

Project implementation strategy combined experiments & computer modeling

The strategy adopted to ensure success of this project was use a combination of laboratory experimental work, along with rigorous process modeling, simulation and optimization. In addition, engineering and economic analysis were being performed at every stage of the project to determine viability. Regular technical meetings were held, in addition to discussions with potential end-users, who provided useful operational guidance.

Experiment was an important component of the project. It provided initial data to commence simulation. However, simulation is key to the success of the project. Most of the existing ammonia plant design did not benefit from process modeling and as such are sub-optimal with high energy consumption, along with operating and capital costs. This project offered the chance to apply computer modeling and optimisation to develop improved ammonia production process.

In this project, process modeling was used to screen process options including flowsheet options and equipment / unit operations configuration. Computer process modeling was also used to optimize and define operating conditions of potential alternatives, as well as to perform sensitivity analysis and the economic evaluation of potential alternatives. Results from the computer simulation also formed the basis for defining and guiding specific experiments for validation, as well as for future design and optimization of the process.

4. Summary of Key Tasks & Findings

Phase 1: KEY Tasks & Findings

This phase of the project is the “*Proof of Concept Stage*”. The key task for this Phase, (the “Proof of Concept Stage”) of the project is to find a potentially suitable adsorbent that would enable separation of ammonia from the synthesis reactor effluent. This has been successfully achieved. The findings are summarized as follows:

- An adsorbent, was found to be suitable for the recovery of ammonia from reactor effluent by pressure swing adsorption (PSA) separation method. Several other adsorbents were screened.

Photograph of Fresh and Used Adsorbent above 300°C

- The equilibrium and kinetic data for the adsorbents were also successfully measured through laboratory experiments. This provided the equilibrium isotherms data for the components.
- A mechanism and the conditions (including the cycle adsorption and regeneration steps) for the optimum PSA separation of ammonia from reactor effluent was also developed.
- The combination of the isotherm data, along with developed PSA cycle separation mechanism enabled the simulation of the process to obtain the optimum conditions. It also enabled the product purity and other process conditions to be predicted.
- Initial economic analysis indicate substantial potential savings in both energy and capital costs. These saves result resulting from i) removal of refrigeration system ii) reduction in natural gas consumption both as fuel and as reactant iii) elimination of recycle recompression and reheating v) reduction in volume or size of key unit operations such as the reformer, shift reactor iv) elimination of other unit operations such the CO₂ absorber, gas scrubbing and methanation units v) complete recovery of ammonia from reactor stream with no wastage through recycle or through purge.
- The successful identification of a suitable adsorbent, along with the development of PSA separation mechanism and optimum conditions from this Phase 1, would enable bench scale PSA experiments to be set up during the Phase 2. It would also enable experimental validation as proposed.

Phase 2: KEY Tasks & Findings

The key task, (the “Phase 2 Go or No Go” decision point) for this Phase of the project is to perform indepth bench scale experiments and analysis on adsorbent(s) performance and stability at similar temperature conditions for the ammonia recovery section. This is critical to enable final choice or selection of suitable adsorbent(s) for the ammonia PSA recovery section. Finding a suitable adsorbent is critical. Another important task is the application of simulation results to guide the construction of the full scale ammonia PSA recovery system. The construction of such a complete and functional system for ammonia recovery is important to enable successful commencement of further studies, experimental data gathering and process optimization for the prototype design and scale up (planned for phase 3) of the project. This key task has been successfully achieved in phase 2.

The findings are summarized as follows:

- Three(3) adsorbents, (names withheld), were successfully found and confirmed (through indepth bench scale experiments) to be most suitable for the recovery of ammonia from reactor effluent by the pressure swing adsorption (PSA) separation method. A total of Ten(10) potentially suitable adsorbents were screened for their performance and sorption/desorption capacity with ammonia.
- Further Bench Scale experiments were successfully performed on stability and irreversibility of the adsorbents with ammonia at temperatures ranging between 50 to 300°C and pressures of 50 to 5000 torr. Unlike the other adsorbents, all these three adsorbents suffered no irreversibility or physical structural damage with ammonia through extensive repeated dynamic cycling at the elevated temperature and pressure conditions.
- The equilibrium and kinetic data were successfully measured and validated through indepth laboratory experiments, covering temperatures ranging between 50 to 300°C and pressures of 50 to 5000 torr.
- Rigorous flowsheet simulation, analysis and optimization was carried out

Ammonia Conversion

Aspen simulation Reactor Conversion Results

- A fully functional ammonia PSA recovery system (with 4-columns, valves, controls and other units) has been successfully constructed. This is the first of its kind for ammonia recovery by psa technology.
- The successful construction of a complete system for ammonia recovery, along with the successful finding of a suitable adsorbent, would enable successful commencement of phase 3 of the project for further studies, experimental data gathering and process optimization for the prototype design and scale up of the project.

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- A mechanism (including the conditions for cycle adsorption and regeneration steps) for the optimum PSA separation of ammonia from reactor effluent was also developed. Further alternative PSA cycle operation steps have been developed, and would be fully analyzed through computer simulation and experimental validation using the newly constructed and fully functional ammonia PSA system.

The constructed full PSA system will enable further studies, additional experimental data gathering, process optimization and detailed validation of simulation results in Phase 3. The resulting experimental data from the PSA system, along with validated engineering data from simulation would be used for the design of prototype and scale up of the ammonia PSA system to industry level in Phases 3 & 4.

Constructed PSA system for Ammonia Recovery

Ammonia Process by Pressure Swing Adsorption

Photograph of Backview of Constructed PSA system for Ammonia Recovery in Operation

Photograph of FrontView

Photograph of System Monitor

The successful identification and validation of a suitable adsorbent, along with the development of optimum mechanism for PSA recovery of ammonia, as well as the successful construction of the full PSA system would enable successful commencement of phase 3 of the project for further studies, experimental data gathering and process optimization. This would enable full validation of simulation results with experimental results, leading to scale-up design of full PSA system during the next phase.

Phase 3 KEY Tasks & Findings

This phase of the project is the process validation of NH_3 PSA Recovery.

The key task, (the “Phase 3 Go or No Go” decision point), for this phase of the project is to successfully test the bench scale ammonia recovery PSA unit and to demonstrate that a high purity and high recovery of NH_3 and H_2/N_2 products are achievable. The economics from the integrated flowsheet compared to conventional is also very important. This “Go or No Go” decision point is critical for two reasons: Firstly, a stable and successful operation of the ammonia psa recovery unit is required to conduct further studies, experimental data gathering and process optimization for the prototype design and scale up of the project. Secondly, the ability to produce high purity and recovery of NH_3 and H_2/N_2 products with the PSA unit is needed as a conclusive demonstration that the new technology can be reliably adopted for the recovery of ammonia from the reactor effluent in the production of ammonia. A strong argument could then be made in the industry for the complete elimination of the energy intensive refrigeration system, currently used in conventional methods of ammonia production and replace them with the more efficient PSA system in both retrofit and green/grass root ammonia plant designs.

The findings are summarized as follows:

- **PSA Equipment Stability:** The constructed ammonia NH_3 PSA recovery system (with 4-columns, valves, controls and other units) was operated and tested over a period of several months from December 08 through August 09. The system has been very stable and has operated well throughout the extensive repeated dynamic cycling at the temperature range from ambient ($\sim 25^\circ\text{C}$) to elevated conditions 300°C and pressure (50 to 5000 torr) conditions.
- **Adsorbent Stability and Performance:** The 4-bed NH_3 PSA experimental system was packed with adsorbent, (which had been selected as one of the top three from previous screening work). The system was operated essentially continuously for several months on the same charge of adsorbent. Numerous PSA runs (more than 30 separate psa runs) were each successfully carried out over a wide range of conditions including different cycle (sorption/desorption) schedules, feed flow rates, cycle times and column temperatures (25 to 300°C) and pressure (50 to 5000 torr) conditions. All runs were allowed to come to the periodic state, which took about 24 to 48 hrs of continuous operation for each run, depending on the conditions. The adsorbent was observed to be very stable, with no signs of adsorbent deterioration. It suffered no irreversibility or physical structural damage with ammonia throughout the extensive repeated dynamic cycling at the elevated temperature and pressure conditions.
- **Experimental Data Gathering:** Further studies and experimental data gathering were successfully gathered from running the PSA recovery system. This data is very valuable for process optimization for the prototype design and scale up of the project.
- **Optimization of PSA Cycle:** A number of alternative PSA cycle operation steps (including different conditions for cycle adsorption and regeneration steps) were analyzed both through computer simulation and experimental validation using the newly constructed and fully functional ammonia psa system. For the 12 best runs, the system was operated using a 12-step heavy reflux PSA cycle schedule at elevated temperatures, feed pressures.
- **High Purity and Recovery Achieved:** The new 4-column PSA experimental runs showed ammonia NH_3 purity of 99.56 % and NH_3 recovery of 99.72 %. This is very comparable to results from computer simulation runs with average ammonia product purity from the new PSA recovery system to be 99.99% NH_3 . This purity and recovery is much better compared to conventional methods.
- The corresponding average composition of the recovered hydrogen/nitrogen stream was H_2+N_2 purity of 98.91 %, and H_2+N_2 recovery of 98.26 %. This means there is so far only about 1% NH_3 along with the H_2/N_2 . This compares much better than conventional methods that recycle 4-6% ammonia, in addition to inerts back to the reactor.

Ammonia Process by Pressure Swing Adsorption

Table: Concentrations (mole fractions) of NH₃, H₂ and N₂ in both the heavy and light products

Run	Recovery NH ₃ in HP (%)	Y _{HP} NH ₃	Recovery H ₂ +N ₂ in LP (%)	Y _{LP} NH ₃
20	99.77	0.9794	91.82	0.0096
18	99.67	0.9790	91.66	0.0137
19	99.49	0.9809	92.43	0.0210
21	99.16	0.9842	93.79	0.0339
17	99.08	0.9826	93.16	0.0370
23	99.72	0.9956	98.26	0.0109
24	99.87	0.9586	83.17	0.0059
25	99.92	0.9336	72.29	0.0043
26	99.92	0.9372	73.86	0.0044
27	99.93	0.9314	71.30	0.0036
29	99.86	0.9689	87.50	0.0060
30	99.50	0.9763	90.57	0.0209

Concentrations (mole fractions) of NH₃, H₂ and N₂ in both the heavy and light products at the periodic state. Recoveries and losses of NH₃, H₂ and N₂ in both the heavy and light products at the periodic state. The recovery of NH₃ corresponds to the fraction of NH₃ fed that was collected in the heavy product; the recoveries for H₂ and N₂ correspond to the fractions of H₂ and N₂ fed to those collected in the light product. The recovery of NH₃ in all cases was greater than 99%. Higher recoveries of NH₃ in the heavy product also led to higher losses of H₂ and N₂ in the heavy product. Run 23 showed the best performance.

- The results from the runs showed a strong and positive effect of increasing the pressure. Therefore more runs are being investigated (at much higher pressures) to further improve the purity and reduce or completely eliminate the ammonia content in the H₂/N₂ mixture. This would be completed by December 2009 for comparative analysis. Any reduction in ammonia content in recycled reactants (H₂/N₂ mixture) would directly lead to enhanced reactor conversion and yield. In addition, higher separating pressure would also means recovered products can be recycled back to the reactor without the need to recompress.

The successful rigorous testing of the 4-column PSA bench-scale prototype, along with the successful production of high purity and recovery ammonia from the system confirms the potential of the technology. Further studies, experimental data gathering and process optimization will enable scale-up design of the full psa system and indepth economic analysis during the next phase. This will strengthen the argument to for the replacement of the conventional methods with the new technology.

Phase 4. KEY Findings and Conclusions (end of Final Phase)

The key findings are summarized as follows:

- New Ammonia Recovery System:** A new Ammonia Recovery system based on the new method was successfully designed, constructed and operated continuously for almost 2years. The system has been very stable and has operated well throughout the extensive repeated dynamic cycling at the temperature range from ambient (~ 25 °C) to elevated conditions 300 °C and pressure (50 to 5000 torr) conditions.
- Adsorbent Stability and Performance:** The new adsorbents used were observed to be very stable, with no signs of adsorbent deterioration. It suffered no irreversibility or physical structural damage with ammonia throughout the extensive repeated dynamic cycling at the elevated temperature and pressure conditions.

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- **Experimental Data Gathering:** Further studies and experimental data gathering were successfully gathered from running the Ammonia recovery system. This data was used for further optimization for the prototype design and scale up of the project.
- **High Purity and Recovery Achieved:** The new Ammonia Recovery system operation produced ammonia NH_3 purity of 99.56 % and NH_3 recovery of 99.72 %. This purity and recovery is much better compared to conventional methods that achieve much less purity 96-98%. The corresponding average composition of the recovered hydrogen/nitrogen stream was H_2+N_2 purity of 98.91 %, and H_2+N_2 recovery of 98.26 %. This means there is so far only about 1% NH_3 along with the H_2/N_2 . This compares much better than conventional methods that recycle 4-6% ammonia, in addition to inerts back to the reactor.
- **Engineering & Economics Analysis:** A process scale-up calculation and corresponding economic analysis¹² were performed. These were done for a typical power plant, assumed to consume about 25tonnes per day of Ammonia. Based on 2010 cost data, the estimated Fixed capital investment (FCI) for the new method was \$2,661,120, made up of purchased equipment and delivery cost was \$528,000, plus \$1,372,800 for installation, Instruments, control, piping, building, facilities, etc and \$760,320 for Indirect Cost. The corresponding total annual energy and raw material (natural gas) cost is \$718,502 per annum. The equivalent conventional method would require Fixed capital investment (FCI) for the new method was \$2,883,360, made up of purchased equipment and delivery cost was \$572,095, plus \$1,487,844 for installation, Instruments, control, piping, building, facilities, etc and \$823,817 for Indirect Cost. The corresponding total annual energy and raw material (natural gas) cost is \$1,902,223 per annum. The New Method would consume 60% less energy than the conventional one.
- These savings result from i) removal of refrigeration system, ii) reduction in natural gas consumption both as fuel and as reactant, iii) elimination of recycle recompression and reheating.

*Newly developed
& successfully operating
Ammonia Recovery System*

5. Potential Application and Benefits

Power/Utility Plants: At least 225 of the 275 of electric utility and power plants in US use ammonia to suppress production of NO_x and to remove CO₂ from burners. Presently, power and utility plants rely on storage of huge amounts of urea or anhydrous ammonia on-site. Ammonia or urea handling or storage is hazardous. Accidental releases of gaseous ammonia by power plants pose a potential danger. There are also logistics problems associated with supply of ammonia.

The new technology is scalable and will enable direct production of ammonia “on-demand or on need” basis. It offers improved safety by eliminating on-site storage and decomposition of urea. It also simplifies supply logistic, (no concerns about running out of supply or inventory) and safety is improved.

Other Ammonia Plants: The new technology can be used for the direct production of ammonia “on-demand or on need” basis in the electric utility and power plants in US that use ammonia. The technology can also be applied to the retrofit of existing ammonia production plants in the USA, which together consume 750 Trillion BTU, (representing more than 10% of total energy in production of the top 50 major chemicals of 7,220 Tril Btu). Our scale-up cost analysis projects a saving of at least 40% in energy consumption, while also achieving a much higher product purity and production.

6. Further Development Work Needed:

The funding so far is focused and directed at developing the new ammonia recovery technology. Beyond the successful demonstration of the new ammonia recovery technology, is the need to integrate with the ammonia reactor section. Through this project, we have identified opportunity to improve the reactor performance, which is key to efficient usage of the Natural gas (and hence overall energy consumptions), and to integrate it together with the new ammonia recovery sections in order to achieve the full potential of the technology. New funding would be required to complete this work.

The objective would be to demonstrate a technically feasible and commercially viable new technology that achieves significant improvement in ammonia synthesis reactor efficiency and is successfully integrated with the ammonia PSA recovery. The outcome would be an integrated technology that can be applied to both green plants process, as well as to retrofit and revamp existing ammonia plants in the U.S and to achieve significant reduction in the energy requirement, raw material usage, capital cost, and environmental burdens while enhancing safety of industrial ammonia production.

7. Conclusions:

A new method has been successfully developed by SmartKoncept Technology and the University of South Carolina to replace conventional methods for ammonia production and recovery. A prototype of the new technology has been successfully built and operated. The new method produces much higher product purity and recovery. More importantly, it reduces energy consumption by more than 40% compared to conventional methods.

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