Executive Summary Final Report: Integrated Chemical Complex and Cogeneration Analysis System: Greenhouse Gas Management and Pollution Prevention Solutions

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Title: Integrated Chemical Complex and Cogeneration Analysis System: Greenhouse Gas Management and Pollution Prevention Solutions
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EPA Project Officer: Bala Krishnan
Research Category: Pollution Prevention

Description and Objective of Research:

Research groups at Lamar University and Louisiana State University have collaborated with an industry advisory group to develop conceptual designs of plants for carbon nanotubes using life cycle assessment and sustainable development criteria for economically viable and environmentally acceptable processes. Developing applications for carbon nanotubes requires the production of pure carbon nanotubes in commercial quantities at affordable prices in environmentally acceptable plants. Presently, the known synthesis methods have limited production capacity, such that the market price of pure carbon nanotubes is of the order of $100 per gm. Consequently, large–scale commercial production based on continuous processes for carbon nanotubes at reasonable costs is essential to emerging carbon nanotube applications.

Summary/Accomplishments:

Research results are summarized below that has been reported in three theses, two journal articles and five conference proceedings. Copies of these documents have been submitted to the Center as specified in the grant agreement and are available from the Center and the authors.

The conceptual design and development of two carbon nanotube production processes: CNT-PFR Process and CNT-FBR Process, with a production capacity of 5,000 metric tons of carbon nanotubes per year (595 kg/hr) each has been completed. This capacity is comparable to a plant producing carbon fibers for composites. The CNT-PFR process reacted iron carbonyl and carbon monoxide in a plug flow reactor (PFR) at 1050 oC and 450 psi with a selectivity of 90% to single wall carbon nanotubes. Purification steps included oxidation, acid treatment and filtration. The CNT-FBR Process reacted carbon dioxide over a cobalt molybdenum catalyst in a fluidized bed reactor (FBR) at 950 oC and 150 psi with a selectivity of 80% to single wall carbon nanotubes. Purification steps included oxidation leaching, froth flotation and acid treatment.

The solution to the material and energy balance equations in the CNT-PFR Process and CNT-FBR process models, the size of process equipments, preliminary design criteria and data for equipment selection, were obtained. Economic decision analysis has been used to estimate the total capital cost requirements for the CNT-PFR and CNT-FBR process models. The net present value (NPV) for the CNT-PFR process was $462.5 million, whereas the net present value (NPV) for the CNT-FBR process was $740.5 million. The net present values for the CNT-PFR and CNT-FBR production processes were both positive, and proposed investment in the production of 5,000 metric tons of carbon nanotubes per year, based on the CNT-PFR and the CNT-FBR production technologies were economically feasible and viable.

The raw materials, products, energy requirements and the emissions from the CNT-PFR and CNT-FBR production processes were obtained The total flow rate of raw materials, which consisted of the feed and other reactants, into the CNT-PFR and CNT-FBR processes, was 3,772 kg/hr and 4,234 kg/hr respectively. The total flow rate of carbon nanotube product and other emissions from the CNT-PFR and CNT-FBR production processes was 3,772 kg/hr and 4,234 kg/hr respectively. The energy consumed by the CNT-PFR and CNT-FBR production processes was in form of steam and electricity. The steam consumed by the CNT-PFR and CNT-FBR processes was 13,746 kg/hr and 18,298 kg/hr respectively. The electrical energy consumed by the CNT-PFR and CNT-FBR production processes was 107 MW and 13 MW respectively. The electrical energy consumed by the CNT-PFR process was significantly higher than the electrical energy consumed by the CNT-FBR process because of the higher operating pressure of the CNT-PFR process (450 psi) compared to the operating pressure of the CNT-FBR process (150 psi).

In summary, the chemical vapor deposition technique offered a more promising route to the commercial production of carbon nanotubes using either a plug flow reactor using iron carbonyl and carbon monoxide or a fluidized bed reactor using carbon monoxide and a cobalt molybdenum catalyst. These reactors were used as a basis for the conceptual design of two commercial–scale plants with a capacity of 5,000 metric tons of carbon nanotubes per year. The plants were designed with recycling unconverted carbon monoxide reactant and purifying the carbon nanotubes. The profitability analysis for both processes showed that both production technologies were economically viable. The economic price for the CNT-PFR process was $38 per kg of carbon nanotubes using a minimum attractive rate of return (MARR) of 25% and an economic life of 10 years. The economic price for the CNT-FBR process was $25 per kg. Based on these results, the route to multi-ton production of high purity carbon nanotubes at affordable prices could become a reality if an environmental impact analysis is positive.

An environmental impact analysis was conducted for both of the CNT processes. Two scenarios were considered: All CO2 released into the environment, and all CO2 reused as raw material. The environmental impact analyses for both the processes were based on the following:

Media for release of CO2, CO and H2 – Air
Water release not accounted for as it is reused: CW/SSS/SST
Efficiency of all heat exchangers: 75%
Only Natural Gas used as fuel
Electricity/Other energy consuming utility was not evaluated

Case 1: All CO2 Released into the Environment: The contribution of each of both the processes in relevant impact categories was determined where quantitative data gives an idea of the magnitude of contribution of each process in various impact categories.

Case 2. All CO_2 Reused As Raw Material: The contribution of each of both the processes in relevant impact categories i was determined where quantitative data gives an idea of the magnitude of contribution of each process in various impact categories.

In summary the environmental impact analysis used two scenarios, and in both it was observed that the water and fossil fuel usage was more in CNT-FBR Process compared to CNT-PFR Process. Moreover, the CNT-FBR Process even contributes to photochemical smog due to the CO released in the environment. Finally, if the carbon dioxide is recycled, the contribution to global warming is eliminated.

In order to provide a more comprehensive impact analysis of these processes, power consumption can be developed for each unit which can be used to back calculate the fuel used for producing it. Most of the streams come out pure (water, product. etc.). In order to provide a more realistic analysis of the CNT production processes, it is necessary to estimate the composition of impurities that would need to be treated before disposal. In the conceptual design, perfect separation was used, and equilibrium composition calculations are needed to improve the results of the environmental impact analysis. Future research will determine more precise details about the composition of process streams.

In general, future research on sustainability is critical for the long-term development of individual industries. Although each individual company is more or less self-operated and self-adapted, due to supply and demand, they are interconnected naturally due to various mass and energy flows. With the evolution of technologies and the emergence of diverse end-products from basic chemicals and materials, the knots among various industrial activities are becoming increasingly tight and complicated, and the economic, environmental, and societal issues are becoming increasingly intertwined. These phenomena occur worldwide, and they are even more intense in some heavily concentrated manufacturing regions. Therefore, such a regional infrastructure can be a good "showcase" for studying sustainability. Particular concern exists regarding the sustainability of highly concentrated areas of chemical and petrochemical industries.

The sustainability of an industrial region including several refineries, two paper mills, and a number of chemical companies which produce both intermediates and specialty chemicals are studied. To properly perform the analysis, both historical and current data on the technical, economic, environmental, and societal aspects are analyzed. To improve sustainability, two types of strategies have been identified and will be delineated in detail. One is for the area industries to work closer together in order to enhance the existing network to effectively utilize all of the available resources, including everything from raw materials to the products and wastes. The other is to embrace new technologies into the existing infrastructure, such as the production of biofuel and nanotechnology.

Publications/Presentations:

Theses and Dissertations

Agboola, Adedeji E., *Development and Model Formulation of Scalable Carbon Nanotube Processes: HiPCO and CoMoCAT Process Models*, M.S. Thesis, Louisiana State University, Baton Rouge, LA, 2005

Singh, Aditi, "*Hierarchical Pareto Optimization and Life Cycle Analysis for Sustainable Development of Large Scale Industrial Ecosystems*," M.S. Thesis, Lamar University, Beaumont, TX August 2004

Smith, Becky, *Analysis of a Petrochemical and Chemical Industrial Zone for the Improvement of Sustainability*, Master Thesis, Lamar University, Beaumont, TX, August 2005.

Aditi Singh, *Hierarchical Pareto Optimization and Life Cycle Analysis for Sustainable Development of Large Scale Industrial Ecosystems*, Ph.D dissertation, in progress, Lamar University, Beaumont, TX, August 2004.
Deblina Sengupta, *Optimal Design of Carbon Nanotube Processes*, Ph.D. dissertation, in progress, Louisiana State University, Baton Rouge, LA, 2006

Journal Publications

Singh, A. and H. H. Lou, "Hierarchical Pareto Optimization for the Sustainable Development of Industrial Ecosystems," in press, Ind. Eng. Chem. Res., 2006.

"LCA for the Evaluation of Different Designs of an Industrial Ecosystem," with Helen H. Lou, Carl L. Yaws and Jack R. Hopper, Journal of Cleaner Production, submitted for publication.
Conference Presentations

Agboola, A. E., R. W. Pike, H. H. Lou, J. R. Hopper, C. L. Yaws and T. A. Hertwig, "Conceptual Design of Continuous Processes for Carbon Nanotubes based on Total Cost and Life Cycle Assessment," Paper No. 289n, Annual Meeting of the American Institute of Chemical Engineers, Cincinnati, (Oct. 30 - Nov. 4, 2005).

Lou, H. H. , R. A. Smith, A. Singh, J. R. Hopper, R. W. Pike and C. L. Yaws "Analysis of a Petrochemical and Chemical Industrial Zone for the Improvement of Sustainability," presented at the AIChE Annual National Meeting , Cincinnati, OH, October 30 - November 4, 2005.

Lou, H. H., A. Singh, R. W. Pike, C. L. Yaws, and J. R. Hopper, "Life Cycle Assessment for the Design of a Large Scale Industrial Ecosystem," invited as a keynote speech at and appear in Proceedings of the *R'05 7th World Congress on Recovery, Recycling and Re-integration*, Sept. 25 - 28, 2005, Beijing, China.

Lou, H. H. , A. Singh, R. W. Pike, C. L. Yaws, and J. R. Hopper, "Life Cycle Assessment for the Design of a Large Scale Industrial Ecosystem," invited as a keynote speech at and appear in Proceedings of the R'05 7th World Congress on Recovery, Recycling and Re-integration , Sept. 25 - 28, 2005, Beijing, China.

Singh, A., H. H. Lou, C. L. Yaws, J. R. Hopper, and R. W. Pike, "Environmental Impact Assessment of Different Design Schemes of an Industrial Ecosystem," in press, Resources, Conservation and Recycling, 2006.

Lou, H. H., R. W. Pike, A. Agboola, A. Singh, X. Li, J. R. Hopper, and C. L. Yaws, "Environmental Impact Assessment For Potential Continuous Processes for the Production Of Carbon Nanotubes," to be presented and to appear in Proceedings of the Air & Waste Management Association 100th Annual Conference, Pittsburg, PA, June 26-29, 2007.

Lou, H. H., R. W. Pike, A. Agboola, A. Singh, X. Li, J. R. Hopper, and C. L. Yaws, "Environmental Impact Assessment For Potential Continuous Processes for the Production Of Carbon Nanotubes," submitted, American Journal of Environmental Science, 2007.

Future Activities: None

Supplemental Keywords: Carbon Nanotubes, Life Cycle Assessment

Relevant Web Sites: www.mpri.lsu.edu