TASK III

Project III.4

DESIGN OF COST-EFFECTIVE WASTE-MANAGEMENT SYSTEMS FOR COAL-LIQUEFACTION PROCESSES

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I. INTRODUCTION

The overall goal of this research program is to systematically design cost-effective waste management systems for coal-liquefaction processes. In particular, two main applications have been targeted: recycle/reuse of gaseous as well as aqueous wastes. The recent strong emphasis on environmental issues provides an additional dimension to the economic viability of coal-liquefaction processes. During the past decade, a number of coal-liquefaction processes have been modified so as to comply with the regulations set for the control of hazardous substances. Unfortunately, these modifications have not followed a systematic approach in design. Hence, these endeavors have been disconnected and the gained insights and expertise have been difficult to transfer from one case to another. While many economic, technical and environmental benefits will significantly accrue as a result of these methodologies, practicing environmental engineers will also be able to transfer waste-recovery technologies systematically and smoothly. The abovementioned challenging tasks call for the development of a novel approach to the design of cost-effective separation networks. Owing to its potential impact on coal-liquefaction technology, such an approach can contribute significantly to the economic competitiveness of coal utilization.

II. SUMMARY OF ACCOMPLISHMENTS:

Since the outset of this project in May, 1992, major findings have been accomplished in designing waste-management systems for the removal of gaseous and aqueous wastes from coal-liquefaction processes. In particular, the following three tasks have been addressed:

1. The removal of hydrogen sulfide from the gaseous emissions of coal-liquefaction processes: A recovery/recycle/reuse approach has been adopted. Hydrogen sulfide, when recovered in its original form or when converted, by reaction, to some other form (e.g. elemental sulfur) may yield products that are reusable or salable. The design of an optimal, cost effective H_2S recovery network is by no means a straightforward task. It requires the simultaneous assessment of various, potentially applicable technologies and separating agents. This realization has led to the recent introduction of the novel notion of synthesizing reactive mass-exchange networks "REAMEN's" (El-Halwagi and Srinivas, 1992). This useful design technique has been employed to screen various potentially applicable technologies and mass-separating agents (both physical and chemical) and to develop a cost effective waste-management system which can reduce the hydrogen sulfide emissions generated in various parts of coal-liquefaction processes to an environmentally regulated level. The optimum system for recovering hydrogen sulfide was found to be a two-stage absorption process in which water is used followed by hot potassium carbonate. The cost of this novel configuration is $1.94/bbl. This cost is significantly less expensive than other desulfurization systems.

2. The removal of phenols from the aqueous wastes of the coal-liquefaction process: One of the most serious environmental problems of coal-liquefaction processes is the generation of phenols in the aqueous wastes. To tackle this problem, a membrane-hybrid system has been devised. This system involves the use of solvent extraction, adsorption and reverse osmosis. In order to identify the optimum configuration of this system, the problem has been formulated as an optimization task with the objective of minimizing the total annualized cost of the system while satisfying all environmental and technical constraints. The result was a membrane hybrid system whose cost is $1.64/m^3 of treated wastewater. This cost is much cheaper than alternate dephenolization schemes.

3. Removal of Carbon Dioxide from Gaseous Emissions: At present, carbon dioxide is not environmentally regulated. Nonetheless, there is a growing trend to impose discharge limits on green-house gases and particularly carbon dioxide. Due to the enormous quantities of carbon dioxide generated within a coal-liquefaction process, efforts have been undertaken to investigate the influence of any future regulation of carbon dioxide on the economics of coal liquefaction. It was found that an environmental specification of 200 ppm will yield an additional cost of about $0.2/bbl. On the other hand, a stringent discharge limit of 30 ppm will result in an additional cost of about $25/bbl.

In the following sections, a more extensive discussion on the findings of this research will be provided.

III. TREATMENT OF AIR EMISSIONS

The major air pollutants from a coal-liquefaction plant are sulfur compounds (H_2S, COS, C_2S and mercaptants), oxides of nitrogen, and carbon dioxide. However, of these, the effects of sulfurous compounds are most deleterious to the environment. The major sulphur compound in the gaseous emissions is hydrogen sulfide. There are three major sources of H_2S from the liquid faction plant. These are the gaseous waste streams leaving the hydrogen generation stage, R_1, that from the gas separation stage, R_2, and from the fractionation stage, R_3. Hydrogen sulfide is known to be toxic and can cause chronic effects in living organisms on long exposures. Therefore the emission levels for H_2S ought to be reduced to an environmentally acceptable level of 5 ppm ($=2.1\text{x}10^{-7}$ kmols/m^3). Hence before these waste gas streams are let to the atmosphere, they have to be treated to bring down the level of H_2S to the acceptable level.

Acid gas treatment technologies that are most commonly employed in industry (Kohl and Reisenfeld, 1985; Astarita et. al. 1983) are (i) absorption into a physical solvent (ii) conversion of acid gas impurities into other chemical forms by chemical solvents and (iii) adsorption on to solids. Based on these methods, several desulfurization processes have been commercially developed. Despite their technical feasibility, the cost of these processes may differ substantially from one case to another. Hence, one should screen all potential processes simultaneously and allow for the possibility of integrating more than one technology. For the design of a desulfurization network to treat the acid gas emissions from the coal plant, eight potential mass-separating agents will be considered which include both physical absorption, chemical absorption and adsorption. These include monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), (all of which are chemical solvents employed in commercial alkanoamine processes), diisopropanolamine (DIAA) (a chemical solvent employed in the ADIP process), hot potassium carbonate (a chemical solvent employed in the Benefield process), physical solvents of water and chilled methanol (employed in the Rectisol process) and activated carbon.

The design of a recycle/reuse desulfurization system for coal-liquefaction plant is based on the procedure of synthesizing a reactive mass-exchange "REAMEN", network (El-Halwagi and Srinivas, 1992). The problem is formulated as an optimization program to minimize the total annualized cost for the given separation task, subject to economic and environmental constraints. The optimization is accomplished via a two stage approach. In the first stage, all potentially applicable technologies and mass-separating agents, are screened simultaneously. The solution of first stage identifies the optimal separation process(es) and the minimum cost of the MSA's involved in performing the specified waste minimization task in a thermodynamically feasible way. This minimum utility cost is solved prior to any commitment to a network structure. The second stage of the optimization strategy is directed toward minimizing the fixed cost of the waste reduction operation by identifying the minimum number of mass-exchange units required for the specified task. The solution of this stage results in identifying the optimal waste reduction loads, stream matches, and thus results in the optimal waste minimization network. Details of this optimization formulation can be found elsewhere (Srinivas and El-Halwagi, 1993; El-Halwagi and Srinivas, 1992).

Based on the aforementioned design methodology, the optimal desulfurization network that is required to perform the required separation task for a 50,000 bbl/day plant at minimum total annualized cost is shown in Fig.1. It involves a single mass-exchange technology, absorption, and employs two different kinds of absorbing agents - a physical solvent, water, and a chemical solvent, hot potassium carbonate. The optimal desulfurization network requires a minimum of five mass-exchanger to satisfy the desired waste reduction duty; two involving water and three involving hot potassium carbonate. The total annualized cost of the optimal desulfurization network is estimated to be \$35.525 x 10^6.

Having solved the problem, it is interesting to compare the optimal solution with other solutions. For instance, one can generate other solutions by using a single MSA only in the network. Hence, the total annualized utility cost for the proposed optimal desulfurization network by using hot potassium carbonate, chilled methanol, DEA, MDEA and activated carbon are 8.41, 46.29, 55.98, 65.71 and 87.90 \$/bbl, respectively. These figures take into consideration the revenue from producing elemental sulfur in the Claus unit, from the stripped acid gases. As indicated by these figures, the optimal solution indeed offers significant cost savings compared to all other configurations.

IV. DEPHENOLIZATION OF AQUEOUS WASTES

One of the most serious pollutants produced by coal-liquefaction processes are phenols. Several technologies may be used to affect the separation of phenols from the aqueous waste streams. These include solvent extraction, adsorption and reverse osmosis. The task of identifying the optimum configuration of this system is quite challenging. One has to simultaneously screen all potential alternatives and identify the minimum-cost system. The problem was formulated as an optimal-synthesis task whose objective is to minimize the waste-reduction cost while satisfying all environmental regulations and technical constraints. The solution has yielded the optimal system shown in Fig. 2. It features a membrane-hybrid system involving solvent extraction, adsorption and reverse osmosis. The cost of this system is \$1.64/m^3 of treated wastewater. This is much cheaper than alternate dephenolization schemes such as aerobic coupling (Chin et al., 1985), solvent extraction (Greminger et al., 1982), and bio-oxidation (Goldstein and Yung, 1977) whose costs are 4.31, 6.42 and 6.47 \$/m^3 of treated wastewater, respectively. These results suggest that the devised membrane-hybrid system can indeed be technically and economically effective in tackling dephenolization problems in coal liquefaction.

V. ECONOMIC IMPLICATIONS OF REGULATING PROCESS CO_2 EMISSIONS

Over the past decade there has been a growing public awareness and concern about the consequences of global warming and the release of "green-house" gases into the environment. Though most of these gases are regulated by the USEPA, there still exists no regulation for the release of CO_2, one of the most dominant green-house gases. However, in light of the mounting public pressures, environmental regulations on the discharge of carbon dioxide may be enacted in the near future. In this regard, it is worth predicting the future of coal liquefaction facilities in the US with respect to the economic implications that may arise as a result of regulating the CO_2 emissions from various parts of the liquefaction plant.

The major source of CO_2 emission from a coal liquefaction facility is from the Claus unit. The acid gas streams entering the Claus unit are rich primarily in hydrogen sulfide and carbon dioxide. While hydrogen sulfide is converted into elemental sulfur in the Claus unit, the tail gases are vented into the atmosphere. This tail gas stream is the single major source of CO_2 process emissions from a coal liquefaction plant. The concentration of CO_2 in this stream can be as high as 600,000 ppm (Noyes Data Corporation, 1980).

As mentioned earlier, there exists several technologies and mass separating agents that can treat gaseous streams containing acid gases. In order to project the economics of reducing process CO_2 emissions to different specifications, five mass separating agents have been considered. These are monoethanolamine (MEA), water, chilled methanol, activated carbon and potassium carbonate solution (30 wt.%).

Based the systematic design procedure discussed earlier, it is now possible to design a reactive mass-exchange network to reduce the CO_2 content in the tail gas stream to different emission specifications. In this work five different emission specifications were selected; 500 ppm, 200 ppm, 100 ppm, 50 ppm and 10 ppm. The results of the optimal operating cost ($/bbl.) required to reduce the CO_2 content in the tail gas stream to these levels is summarized in Fig. 3. It can be seen that while the cost to reduce the carbon dioxide content to 500 ppm is essentially negligible ($ 0.10 - 0.20/bbl.), the operating cost increases exponentially as the emission specification is reduced and finally becomes asymptotic as the level drops to 10 ppm. A similar trend is observed for treating tail gas streams of different flowrates (Fig. 4).

VI. CONCLUSIONS

Several systematic procedures for designing optimal waste management systems for coal-liquefaction processes have been developed. These procedures were used to identify cost effective solutions for two major environmental problems associated with coal liquefaction; desulfurization of gaseous emissions and dephenolization of aqueous wastes. The generated solutions enjoy noticeable technical and economic merits over alternate configurations proposed in literature. In addition, these techniques were used to assess the impact of any future regulations of carbon dioxide on the economics of coal liquefaction.

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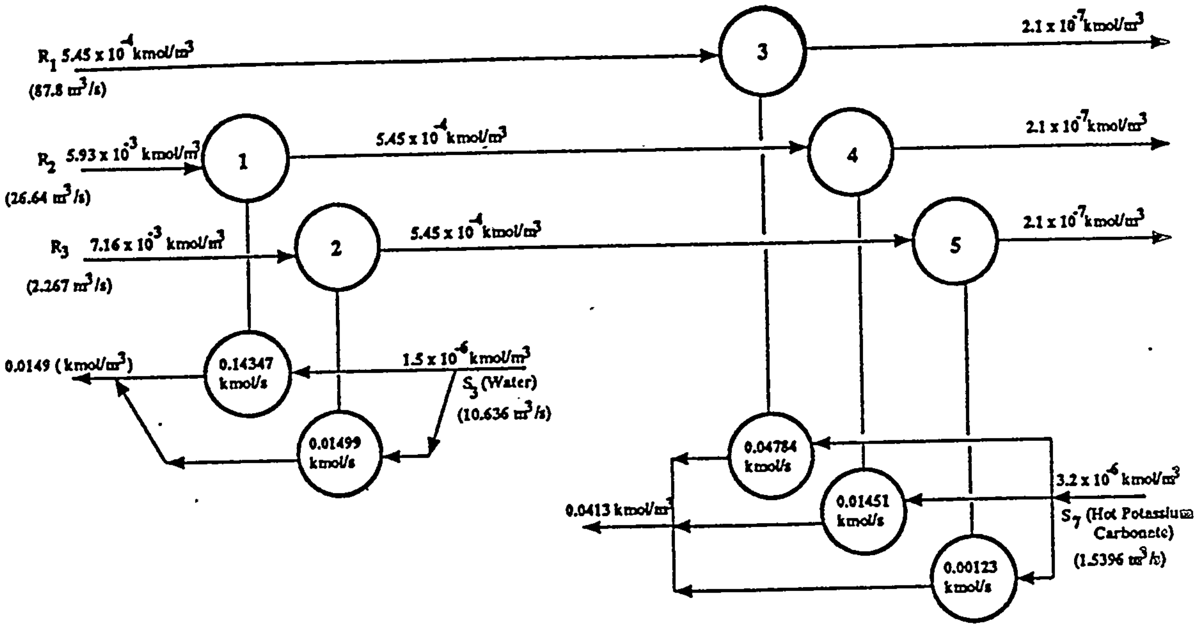

Fig. 1. Optimal Desulfurization Network

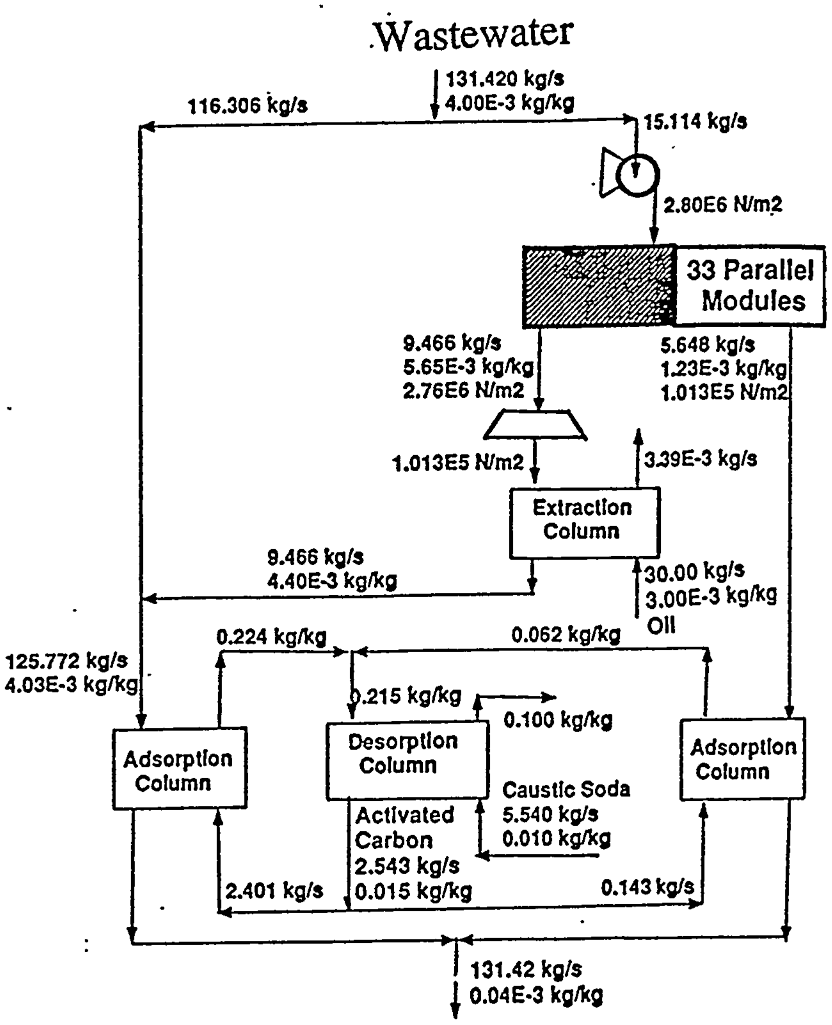

Fig. 2. Optimal Dephenolization Network

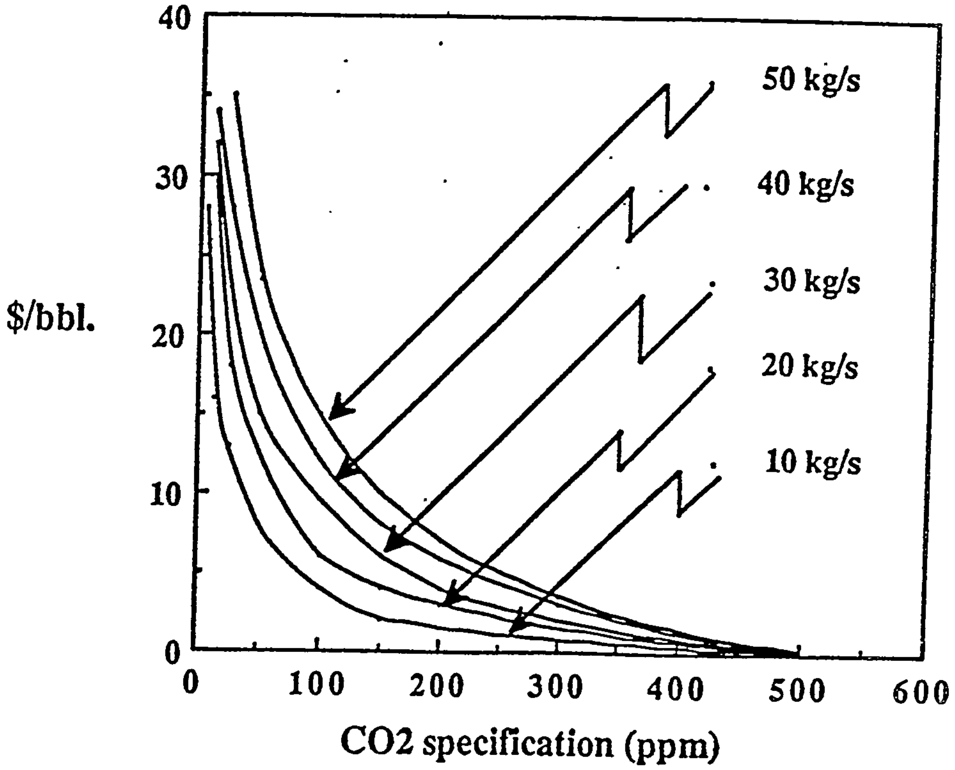

Fig. 3. Economic Implications of Regulating Carbon Dioxide