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MEMBRANE / DISTILLATION HYBRID PROCESS RESEARCH AND DEVELOPMENT
Phase II

Final Report

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Executive Summary

This report covers work conducted under the grant awarded to BP by DOE in late 1991 entitled "Membrane / Distillation Hybrid Process Research and Development." The program was directed towards development and commercialization of the BP process for separation of vapor phase olefins from non-olefins via facilitated transport using an aqueous facilitator. The program has come to a very successful conclusion, with formation of a partnership between BP and Stone and Webster Engineering Corporation (SWEC) to market and commercialize the technology. The focus of this report is the final portion of the program, during which engineering re-design, facilitator optimization, economic analysis, and marketing have been the primary activities.

At the end of Phase II BP was looking to partner with an engineering firm to advance the selective olefin recovery (SOR) technology from the lab/demo stage to full commercialization. In August 1995 BP and SWEC reached an agreement to advance the technology by completing additional Phase III work with DOE and beginning marketing activities.

The summary is followed by detailed task reports for Tasks 1, 5, and 6 and Appendices I-IV.

TASK 1.: Economic Evaluation .

Early in Phase III of the program a comparison was made between membrane contactors and conventional contactors for absorbing ethylene into the facilitator solution. Conventional contactors were considered capable of overcoming problems encountered in the Toledo and Grangemouth demonstration units due to membrane fouling and degradation. Economic evaluations carried out by Stone & Webster Engineering Corp. showed that cheaper flow schemes resulted when the membrane contactor was replaced by a conventional absorber. Moreover, the process operability was projected to be higher due to fewer problems arising from membrane fouling. On this basis savings in a 350,000 MTA grassroots olefins plant with the FT technology was calculated to be 32% on capital and 18% on operating costs over conventional technology. Further design, analysis and experimentation was then confined to the new absorber/stripper design rather than the membrane process.

TASK 2: Process Design Manual - Propylene Splitter.

TASK 3: Process Design Manual - Polymer Vent Gas.

Both Tasks 2 and 3 were initiated based on the assumption that application to C3 splitters and polymer vent gas would be the first commercial niches for a membrane FT process. Re-engineering of the process from a membrane to an absorber column showed that higher process reliability and competitive economics were possible. In light of this analysis the tasks to produce process design manuals based on the membrane process was deferred indefinitely. SWEC will be addressing these important functions as part of the non-DOE funded continuing program.

TASK 4: Technology Development - Terry J. Mazanec / Stone and Webster Engineering Corp.

BP and Stone and Webster have agreed to continue a commercialization effort extending beyond the termination of the DOE program. As part of the commercialization effort, a customer has been identified to use the Toledo demonstration unit in a commercial chemical plant. The unit has been made ready for transfer and moved from its Toledo siting. This unit will be used for ethylene separation from an ethylene oxide vent gas, and as a working demonstration plant for customer visits and evaluations. More units of this scale are expected to be constructed and sold as the project moves forward. Another part of the commercialization effort is the design and construction of a large scale demonstration of the process for cracked gas recovery, which is under consideration for a BP site. Details of the Task 4 activities can be found in Appendices I-III.

TASK 5: **Advanced Cu(I) Facilitators** - Prof Bruce Averill / Terry J. Mazanec

Facilitators under consideration for the process included the silver nitrate used in the demo units, a copper nitrate-pyridine solution, and novel copper-based materials capable of selectivity in separating olefins under development by Prof Bruce Averill at the University of Virginia. As the engineering studies progressed it was recognized that separating ethylene from propylene could best be done conventionally. Since the advanced facilitator work was focused on developing facilitators for ethylene/propylene separation and that function was no longer needed, further work at UVA was concluded.

TASK 6: **Facilitator Testing** - Terry J. Mazanec.

Considerable work was done to advance and optimize the copper-pyridine solution due to the reduced metal cost with a Cu-based compared to a Ag-based system. However, the additional recovery equipment needed, lower capacity, and possible hazards associated with pyridine make the copper system more costly to operate. Flawless demonstration of the absorber/stripper mode of the selective olefin recovery (SOR) process was achieved in a bench scale, glass, continuous recirculating reactor. Tests ran some 200 hours with stripper pot temperatures as high as 100 C, confirming the stability of the solution demonstrated in batch reactions.

The present DOE program has been an unqualified success. BP and SWEC have transformed a laboratory scale process, which had been demonstrated with a membrane contactor, into a commercial venture that is resulting in license income, plant construction, and energy efficient operation in olefins separation. Widespread implementation of the BP selective olefin recovery process by chemical producers and refiners will produce substantial energy savings for some of the Nation's largest, most energy intensive industries.

Introduction

Petrochemicals production is a capital intensive commodity business with a steep entry barrier to new technologies. Producers need to minimize risks associated with new technologies in addition to realizing substantial incentives from energy savings and improved olefin recovery efficiencies. A successful pioneering effort will be needed to convince producers of the practicability of a revolutionary technology like facilitated transport separators. The facilitated transport technology has the best chance to penetrate the olefins market by a step-wise introduction, starting with narrow niche applications and proceeding to broader chemical and refinery complexes.

BP Chemicals (BPC) recognizes that within its own business operations it has a limited number of opportunities for commercializing olefin separating processes. In order to increase the likelihood of matching the facilitated transport technology to its most favorable niche application BP Chemicals has pursued a partnership with an engineering firm that supplies technology to the petrochemicals industry. After evaluating several firms, a suitable partner was found in Stone and Webster Engineering Corporation (SWEC). Stone and Webster is a large international supplier of technology and engineering services to petrochemicals producers of all types. SWEC has designed/constructed over 100 units worldwide, representing one-third of the world's ethylene capacity. Stone and Webster has a strong track record of pioneering new olefins technologies, including ultraselective conversion, advanced recovery systems, cryogenic demethanization, dilution steam recovery, and isothermal hydrogenation. The BPC/SWEC partnership puts the program in a better position to enable market entry through SWEC's extensive contacts within the industry and commercial arrangements with numerous producers.

BP Chemicals and Stone and Webster have developed a vision for commercialization of the facilitated transport (FT) technology that has both short term and longer term components. In the short term there is a growing demand to expand the capacity of olefin splitters and olefin recovery from waste streams in response to the strong recovery of the petrochemicals business in 1994. This growth in demand can open a commercial niche for FT systems which will engender acceptance of the facilitator technology within the industry. In the longer term, facilitators are seen as more advantageous on a large scale if they are operated as absorber/stripper units that can recover ethylene and propylene from raw cracked gas in new olefins plants.

The technical feasibility and economics for the longer term application to olefin recovery in cracked gas or other large scale olefins plants is critical to the long term acceptance of the technology. Preliminary process scheme development and conceptual engineering explored absorber/stripper schemes that may be more favorable for such large-flow applications. The objective was to determine the feasibility of the absorber/stripper concept in order to focus laboratory research and development efforts.

Detailed reports for Tasks 1, 5 and 6 follow. Tasks 2 and 3 were deferred. Details for Task 4 are contained in Appendices I-III.

TASK 1.: Economic Evaluation - Stone & Webster Engineering Corp.

Summary

Stone and Webster have completed a first pass comparison of the facilitated transport (FT) technology used in an absorber/stripper design compared to conventional technology for ethylene recovery from a gas cracking plant. Estimates show that the FT process achieves about a 19% reduction in capital, a 55% reduction in shaft power, and a 60% reduction in heat requirements. The bulk of these advantages are attributable to elimination of the refrigeration system.

Stone and Webster have refined the study of the facilitated transport (FT) technology used in an absorber/stripper design compared to conventional technology for ethylene recovery from a gas cracking plant. In a 350,000 MTA grassroots plant the savings with the FT technology is calculated to be 32% on capital and 18% on operating costs. Evaluation of a 150,000 MTA expansion of BP's ethylene plant in Scotland showed that a 20% capital savings could be obtained but that operating costs could be 50% higher to 20% lower depending on assumptions.

More detailed site-specific economics have been prepared for a membrane unit at a customer's Gulf Coast ethylene oxide plant. Favorable payback times were calculated using the silver based Toledo-style units.

Updated economic evaluations of a grassroots gas cracker fitted with an absorber/stripper olefins separation process were prepared with high olefins recoveries (98% ethylene and 90% propylene). Capital cost savings of 30-34% and operating cost savings of 16-20% for a 350,000 tpa plant were calculated for various absorber pressures. Using the new technology plants can be made as small as 150,000 tpa and still give economics comparable to a large scale plant using conventional technology.

Details of these economic evaluations are to be found in Appendices I-III.

TASK 5: Advanced Cu(I) Facilitators - Prof Bruce Averill.

Summary

Development of a multidentate ligand for stabilization of Cu(I) complex capable of discriminating among various olefins on the basis of size was pursued. The best ligand identified was a pentamethyldiethylenetriamine, Me5-dien. Characterization of the complex by H and C NMR was carried out to establish ethylene absorption/desorption kinetics, and an X-ray structure of the ethylene adduct was determined. Ethylene is displaced from the Me5-dien complex by acetylene or by thiols, as expected. The complex appears suitable for olefin facilitator studies provided ethylene uptake rates and ligand cost concerns are addressed.

Results and Discussion

A pure salt of a copper-triamine-ethylene complex was needed for use as the benchmark in ethylene binding studies. Efforts were directed at obtaining microcrystalline samples of an ethylene adduct of copper(I)-diethylenetriamine as the nitrate salt. However, high solubility of the nitrate salt in the preparation solution prevented its selective precipitation with most cosolvents. A tetraphenylborate salt is known, but its water insolubility make it impractical as a benchmark.

A simple synthetic route to pure solutions of the target chelated Cu(I) complex, $[Cu(dien)(C_2H_4)]NO_3$, was developed. A disproportionation reaction between copper metal and Cu(II) nitrate in the presence of the dien ligand and an excess of ethylene proceeds smoothly to generate the desired complex. However, during characterization studies of the complex it was noted that upon removal of the Cu(0) source the disproportionation reaction can slowly reverse itself to give the undesired Cu(II) complex, $[Cu(dien)(NO_3)]NO_3$ and Cu(0). These results suggest that the combination of the highly basic tridentate dien ligand with certain anions is intrinsically unstable in aqueous solution. Attempts to replace the nitrate anion with sulfate were unsuccessful due to poor solubility; at least one other anion will be assessed.

A variant of the chelate dien ligand with five methyl groups replacing the amino hydrogens, Me5-dien, was tested in the hope that the increased size of the methyl groups would prohibit formation of the adduct responsible for disproportionation. Indeed, solutions of the complex formed by the reaction of Cu(II) nitrate, Cu metal and two equivalents of the Me5-dien ligand with an excess of ethylene were stable for days in the absence of O2. The complex, $[Cu(Me5\text{-}dien)(C_2H_4)]NO_3$ is apparently so soluble in methanol that a change of solvents to isopropanol was needed to prepare crystalline samples. The enhanced solubility could prove beneficial to preparing solutions with high olefin capacities.

A fully refined crystal structure of $[Cu(Me5\text{-}dien)(C_2H_4)]NO_3$ was completed including the positions of the interacting H atoms on the ethylene and the ligand. Analysis of the structure should lead to a better understanding of the control of ethylene binding by inducing steric hindrance. Experimental evidence was obtained demonstrating the suitability of the Me5-dien complex as a facilitator. The ^1H and ^{13}C NMR spectra of the ethylene adduct, $[Cu(Me5\text{-}dien)(C_2H_4)]NO_3$, measured over the temperature range -83 to +57 C in d4-MeOH showed that the bound ethylene was exchanging with added free ethylene. The temperature dependence of the spectra suggests rapid exchange between free and bound ethylene, with a rate estimated to be about 1000 s^{-1} at 57 C. The mechanism of exchange is expected to involve dissociation of ethylene as the first step; support for this comes from the absence of a concentration dependence in the NMR study. This is an important finding that suggests that olefin exchange will not be complicated by ligand reactions, e.g. the complex is stable under olefin exchange conditions.

From ^1H and ^{13}C NMR spectra of the ethylene adduct, $[Cu(Me5\text{-}dien)(C_2H_4)]NO_3$, in d4-MeOH the equilibrium constant for ethylene dissociation was calculated to be 6.1×10^{-3} at 17 °C in the absence of added ethylene. Under 1 atm of ethylene pressure the temperature dependence of the spectra is very complex. Initial assessment of the spectra indicate that the intermediate may be a complex containing two molecules of ethylene bound to the metal at higher temperatures and higher ethylene concentrations. The long Cu-N bond observed in the crystal structure may be breaking to accommodate the extra ethylene ligand.

The ^{1}H NMR spectra of the ethylene adduct of the Me5-dien complex show clearly the presence of two distinct ethylene complexes in the presence of 1 atm of ethylene. The first is believed to be the expected adduct, while the second complex is thought to be one in which the weakest Cu-N bond observed in the crystal structure of the parent complex is breaking to accommodate the extra ethylene ligand. NMR spectra of the Cu(I)/3-hydroxy-pyridine/ethylene complex have been obtained showing a clean resonance from coordinated ethylene, suggesting that the affinity of the 3-hydroxy-pyridine complex is higher than that of the Me5-dien complex.

The Me5-dien complex, $[Cu(Me5\text{-}dien)(C_2H_4)]NO_3$, has been observed to react with acetylene to form a red precipitate, even when acetylene pressures are as low as 5×10^{-4} atm of C_2H_2. Reaction of the complex with n-dodecanethiol, a non-volatile model for H_2S and thiols results in destruction of the complex by formation of a precipitate even at Cu/RSH ratios as high as 100.

TASK 6: Facilitator Testing - Terry J. Mazanec.

Summary

The Selective Olefin Recovery (SOR) process employs a metal ion facilitator solution to absorb olefins from mixed gas streams. Early work concentrated on aqueous $Ag(NO_3)$ solutions, and two demo plants were successfully operated with the Ag system and hollow fiber membrane contactors. Larger applications require cheaper facilitators and absorbers to reduce capital costs. Valus found that water solutions of cuprous salts with nitrogen ligands were good facilitators for olefin separation, but the systems were not thoroughly studied. His best solution was a 2 M aqueous cuprous nitrate with 2 equivalents of pyridine.

This work was undertaken to demonstrate the technical feasibility of using Cu(I) solutions for olefin separations, with the specific goal of finding a suitable ligand with lower vapor pressure than pyridine to minimize ligand losses in continuous operation. Ethylene capacity experiments involved measuring the amount of ethylene absorbed by batch solutions of the desired complex in water with 2M Cu and L/Cu ratio = 2.1. The solutions were prepared by mixing equal portions of Cu^O and $Cu(NO_3)_2$ with the appropriate ligand in water. Numerous pyridine derivatives were tested as ligands and 3-pyridylcarbinol was found to complex with Cu(I) to give solutions with ethylene capacities equal to those of pyridine (28 cc/cc). However, it was observed that all of the $Cu(I)(NO_3)$ / ligand solutions were unstable to irreversible formation of a red-orange solid. This solid was tentatively identified as cuprous oxide, Cu_2O.

Optimization of the py/Cu ratio and Cu(I) concentration was attempted using the pyridine copper nitrate solution. Capacity for ethylene absorption was measured over the range of L/Cu ratios from 2.1 - 3.0 for 2 M Cu solutions. Maximum ethylene uptake of 29 cc/cc was observed at L/Cu ~ 2.25, and as L/Cu was increased the capacity dropped linearly to 19 cc/cc at py/Cu = 3. Measurement of ethylene uptake of solutions with [Cu] of 1, 2, 3, and 4 M with py/Cu = 2 showed uptakes of 10, 16, 28, and 50 cc/cc, respectively.

In addition to capacities, ethylene uptake rates were measured for all of the solutions. Most of the solutions took up ethylene at the feed rate (~0.6 cc/cc/min) until near the saturation point, when the uptake rates dropped to a low level for a while before complete saturation occurred. For the base case (2 M Cu, 2py/Cu) uptake was fast for 30 minutes and then slower for an additional 40 minutes. Solutions of the best pyridine substitute ligand had significantly slower ethylene uptakes after only 10 minutes, but still had capacities about equal to their pyridine analogues. Excess Cu(II) nitrate had little effect on ethylene uptake rate or capacity.

Suppressing formation of the red-orange solid was designated as a priority for demonstrating process feasibility since it would cause problems during commercial operation. The solid was postulated to form by dehydration of an intermediate hydroxide complex, e.g. $2\ \text{'Cu(OH)'} \Rightarrow Cu_2O + H_2O$. Solvents with available oxygen atoms, such as, ethylene glycol, glyme, diglyme, and 1,4-dioxane were investigated as a means of blocking hydroxide formation, with no success. Adjustment of pH by addition of HNO_3 proved effective in preventing formation of the orange solid. A solution of 2 M Cu(I) with $Cu/py/HNO_3$ ratio = 1/3/1 was heated to 80 C for 270 hours without loss of ethylene uptake and with no evidence of formation of copper oxides. When the $Cu/py/HNO_3$ ratio was adjusted to 1/2.75/1 the capacity was ~22 cc/cc, and the solution could be heated to 80 C for over 440 hours with no solids formation. In both of these cases the solution solidifies into a light blue gel when the ethylene-free solution is permitted to cool below about 40 C; the solid could be easily redissolved by gentle heating or admission of ethylene. Separate tests showed that > 0.15 atm of ethylene pressure was sufficient to inhibit solidification. The pH of these solutions was about 3.5.

Continuous demonstration of the absorber/stripper mode of the SOR process using the stabilized Cu/py/HNO_3 was achieved in a bench scale, glass, recirculating reactor. The reactor can handle up to about 300 cc of facilitator solution and separate up to 100 sccm of ethylene. With a recycle pump rate of some 60 sccm, steady removal of >90% of a 50 sccm feed of ethylene was measured. Separation of ethylene from nitrogen and ethane was demonstrated, as was the recovery of propylene. Olefin/paraffin separation ratios were measured as 50-100. Several tests ran over 200 hours with the stripper pot immersed in an oil bath with temperature as high as 100 C without the formation of solids, confirming the stability of the solution demonstrated in batch reactions. This is the first continuous demonstration of the absorber/stripper concept with an aqueous Cu-based facilitator.

BACKGROUND

In a facilitated transport process an olefin containing stream is contacted with a solution of a metal complexing agent, or facilitator, that absorbs the olefin. The olefin containing solution is separated and sent to a second vessel where the olefin is removed by increasing the temperature or reducing the pressure. Then the lean solution is returned to the contactor. A schematic is shown in Figure 1.

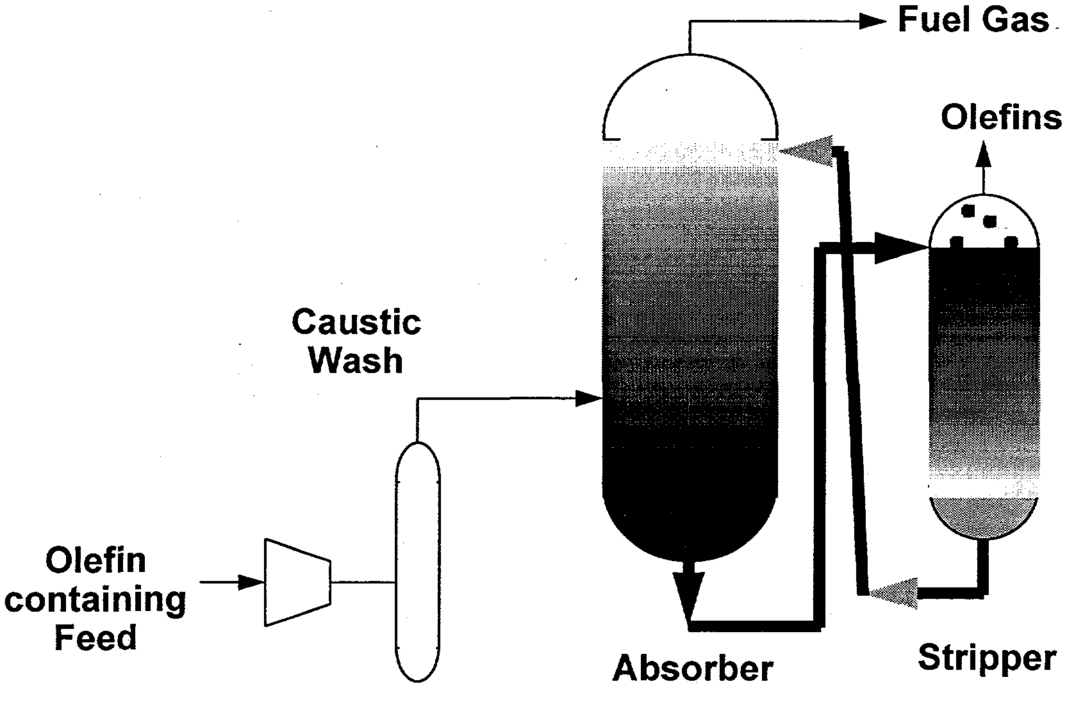

Figure 1. Schematic of an Absorber/Stripper Process

Olefin separation via facilitated transport has been under investigation at BP for several years. Most of the work focused on the use of $AgNO_3$ as the complexing agent in water solution using hollow fiber membranes. Initially the fibers were designed to act as true membranes where the olefin would be passed to the interior due to its greater affinity for the Ag absorbed in the membrane pores. When it was discovered that the membrane rapidly dehydrated, the facilitator solution was circulated through the hollow fibers, using them as a high surface area gas/liquid contactor. A grant from the USDOE was obtained in 1991 to partially support design, economic analysis, facilitator development and engineering work on the process. Two demonstration plants utilizing the technology were constructed and operated successfully. A demo plant at Toledo Refinery was designed to debottleneck a C3 splitter and the demo plant at Grangemouth, Scotland was used to recover ethylene from ethanol offgas. It was recognized that the economics of the process would be improved, particularly for large scale installations, by replacement of Ag with a cheaper metal. Valus and Davis briefly explored Cu(I), which had been used for a short time in a commercial hydrocarbon based olefin recovery plant in the 50's. They determined that an aqueous Cu(I) solution with nitrogen ligands such as pyridine absorbed significant quantities of olefins. However this preliminary work stopped when they left BP in 1994.

In 1995 BP Chemicals came to agreement with Stone and Webster Engineering Corp. (SWEC) to jointly advance the technology now called Selective Olefin Recovery, or SOR. SWEC was to take responsibility for marketing the membrane process demonstrated at Toledo and Grangemouth and for engineering and economic studies on an absorber/stripper concept being advanced by BP Chemicals Olefins Division. BP Chemicals was to focus on developing engineering data for absorber/stripper applications to cracked gas purification in the UK, and on stewardship of the DOE program and development of the Cu(I) facilitator in the US. The absorber/stripper concept replaces the membrane contactor used in the demo plants with a conventional liquid/gas contactor column to absorb olefins from the feed gas mixture. The stripper would remain a conventional column operated at higher temperature and lower pressure to desorb the olefins as it had been in the demo units. Vapor liquid equilibrium (VLE) data were needed and the chemistry of the Cu(I) complex was poorly understood.

The present work was undertaken to demonstrate the technical feasibility of using aqueous Cu(I) solutions for olefin separation, with the specific goal of finding a suitable ligand with lower vapor pressure than pyridine to minimize ligand losses in continuous operation. Very early on it was found that solids precipitated from the Cu(I) solutions that could render the process commercially unworkable; prevention of solids formation became an urgent goal of the project. This report documents the work on the chemistry of the aqueous Cu(I) facilitator solutions performed at Warrensville from January to September, 1996.

Preparation of Copper Complex

The copper(I) complex is prepared by adding copper wire, copper(II) nitrate hydrate, water, and the ligand (and concentrated nitric acid in some experiments) to a helium or nitrogen purged three neck flask. For single pot studies the flask is equipped with a gas inlet adapter, condenser with gas outlet adapter, and a stopper. For continuous absorber/stripper experiments the flask is equipped with a condenser, an adapter with the dip tube that leads to the liquid pump, and a liquid leveling device with gas purge. In all cases the liquid in the flask is stirred magnetically; however, the stirring is stopped in the recycle reactor once the liquid pump is started.

Standard 2 M $CuNO_3$ / 2.75 Pyridine / 1 eq. HNO_3 Preparation In The Recycle Reactor

Copper wire (12 g, 0.19 mol) is added to a purged three neck flask which will serve as the stripper pot, and a stir bar is added. The $Cu(NO_3)_2$-2.5 H_2O (48.75 g, 0.19 mol) is added to 124 ml of distilled water. After all of the nitrate has dissolved this solution is added to the copper wire while helium purge is maintained. The pyridine is then added (87 ml, 85.4 g, 1.08 mol). The solution warms slightly during the pyridine addition. After stirring ~ 1 hour the concentrated nitric acid is slowly added (34.2 g of 70% HNO3, 0.39 mol). **Caution!! This reaction is very exothermic.** It takes 1-2 minutes to add the acid and the mixture heats up to about 60 C. Stirring is maintained as the deep blue solution is permitted to cool. Before recycling the liquid, the stirrer is turned off.

Continuous Absorber/Stripper Operation

Figure 2 presents a schematic diagram of the glass continuous absorber/stripper apparatus. While the solution still contains predominately Cu(II) as indicated by its deep blue color and the remaining copper wire, the liquid pump is set to the desired flow and started. The liquid is pumped to the top of the absorber column where it flows downward through the column countercurrent to the hydrocarbon gas flow. In some experiments the absorber column is filled with glass or ceramic beads to enhance gas/liquid contact. The olefin containing gas stream is fed in through the bottom of the absorber and travels up the column. At the top of the column there is a vent for unabsorbed gases to be measured or collected. The copper-olefin complex drains from the bottom of the absorber column through a Teflon® tube into a liquid leveling device. This device is a Teflon® tube that is fitted to an adapter where it can overflow into the original three neck flask which is the stripper. The liquid level in the absorber column can be adjusted by simply raising or lowering the leveling device; this also adjusts the relative amounts of liquid in the absorber and stripper. The liquid overflows into a short column to begin gas/liquid separation. Carrier gas (He) is fed into the top of this column to reduce the effective pressure of olefin in the stripper and to provide momentum to turn the dry test meter during very low flow experiments. The stripper pot is heated to de-complex the absorbed olefin, which is carried from the flask to the vent for samples collection and flow measurement. Gas flows are measured with a dry test meter or a bubble meter. Gases are analyzed using a Carle GC fitted for Refinery Gas Analysis.

Observations on the Continuous Absorber/Stripper Operation

- The transfer line from the pump to the absorber top is heat traced and kept around 40C. This line transfers lean solution which when cooled below 35C with less than 0.15 atm olefin partial pressure the complex tends to solidify. However, if a solid plug does form it is easily removed by introducing ethylene (you can actually watch the solid liquefy as the olefin contacts the solid), or the solid can be warmed with a hot air gun until it liquefies and starts to flow again.

- Solutions containing copper (II) are dark blue, whereas the copper(I) solution is a light green. When ethylene is absorbed by the Cu(I) complex the solution becomes a slightly darker shade of blue-green. When large amounts of olefin are being absorbed and desorbed in this process the state of the Cu(I) complex can be determined by comparing the colors of the Teflon® transfer lines leading to and from the stripper pot.

- The flow of olefin through the absorber is easily monitored by watching the bubble stream decrease. If desired the olefin feed rate can be adjusted to the point that essentially no olefin leaves the top of the absorber. This allows quick maximization of olefin absorption at the given liquid feed rate.

- If an air leak forms in the system it is readily apparent as the solution color changes from light blue-green to a darker blue. The copper complex can be regenerated by adding more copper metal to the system, which affects the concentration of the copper(I) species.

- The copper (I) complex forms much faster in the presence of nitric acid than without acid. As little as four hours can give enough copper (I) in the presence of nitric acid to start ethylene absorption. Whereas it would take about 24 hours to give nearly the same absorption results in the absence of nitric acid.

- While investigating the effect of ligands on ethylene absorption, the ethylene was removed by heating the solution for only an hour or so at a time and then cooling before reintroducing the ethylene. During the solids formation studies, the complex was maintained at the high temperature for days before cooling. In general the complex spends 1-2 minutes in the stripper pot during recycle runs. No solids have been observed yet in the recycle reactor while using the nitric acid composition.

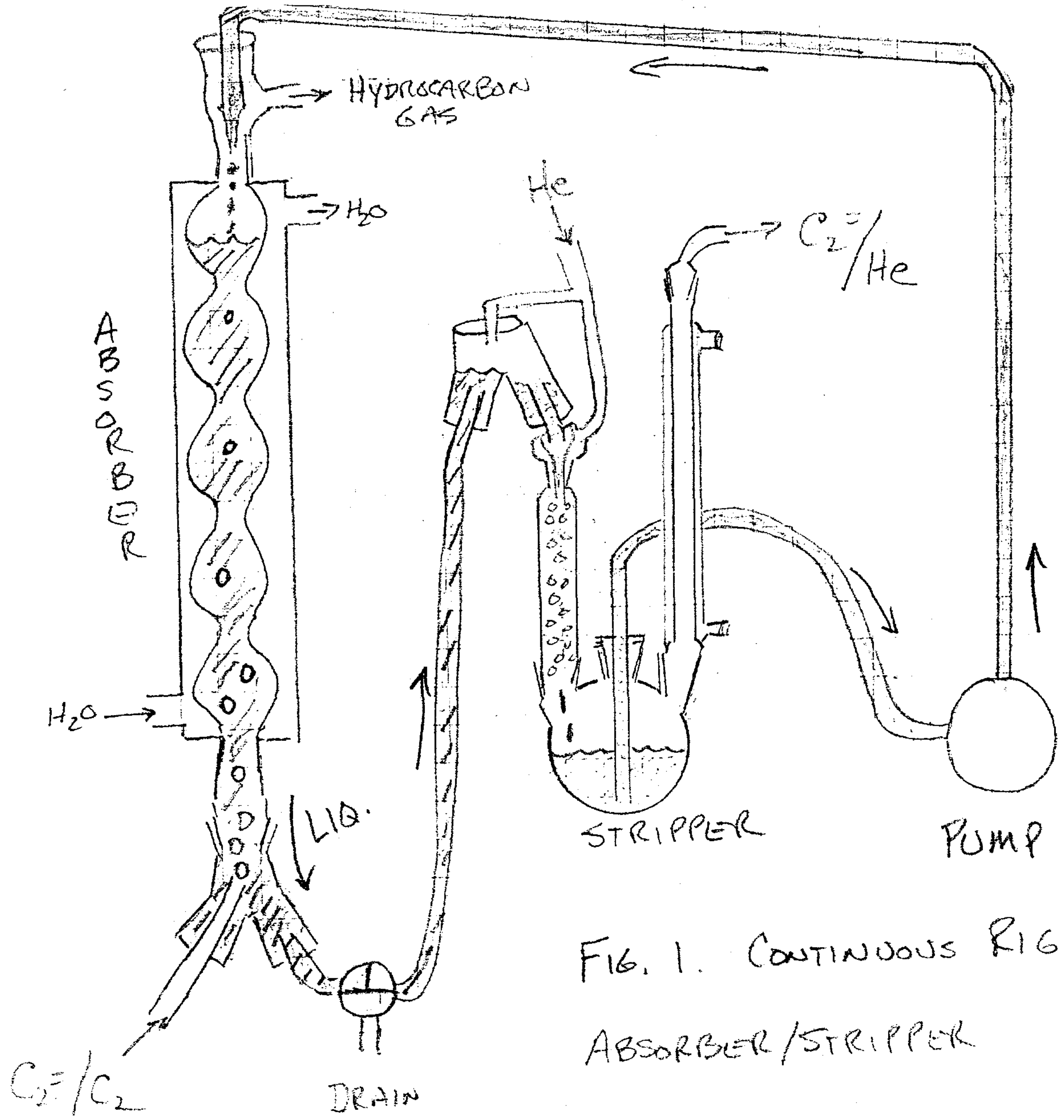

FIG. 1. CONTINUOUS RIG - ABSORBER/STRIPPER

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Figure 2. Schematic of Glass Continuous Absorber/Stripper Apparatus

- Absorbed carbon monoxide has a similar effect as absorbed ethylene: it inhibits the reversible solid formation. In the case of ethylene when the absorbed ethylene concentration drops below 15% and the temperature drops below 35 C a solid forms. The amount of absorbed CO required to keep the complex from forming this reversible solid has not been determined.

RESULTS AND DISCUSSION

Substitute Ligands in Cu/py Facilitators

In the absorber/stripper design the facilitator solution is heated to about 80C to decomplex the olefin. During the heating a significant amount of pyridine could be entrained in the product due to its appreciable vapor pressure at 80 C (pyridine bp = 115 C), and its tendency to form a 1:3 py:H_2O azeotrope that boils at 92-93 C. A variety of nitrogen ligands were tested as substitutes for pyridine in the Cu(I) facilitator solution with the aim of minimizing what is expected to be significant ligand loss. These ligands were chosen for their higher boiling points and their water solubility. In general it is believed that oxygen containing functional groups like hydroxyl, or carboxyl, would both raise the boiling point and maximize solubility. A third consideration is their hydrophilic character. It is thought that hydrophilic ligands would minimize alkane solubility thus enhancing olefin selectivity whereas hydrophobic ligands would increase alkane solubility thus reducing olefin selectivity. One of the key advantages of an aqueous facilitator is its selectivity for olefins and low solubility of paraffins. The structures of the various ligands are shown in Figure 3.

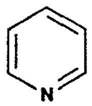
Table 1 summarizes the results with ligands tested as substitutes for pyridine. The data in the table are median points of several absorb/desorb cycles, and for a few ligands there was considerable scatter. With pyridine the uptake typically increased from its first measurement to a 'steady state' value after one cycle. This was believed to be due to slow disproportionation of Cu(0) and Cu(II) to form the Cu(I) complex. Occasionally after several cycles the capacity would decline, and this was believed to be due to oxidation of Cu(I) to Cu(II) by air that leaked into the system. Of all the ligands tested **only 3-pyridylcarbinol proved an adequate substitute for pyridine in terms of capacity**, with capacity of 28 cc ethylene absorbed per cc of facilitator solution. With the carbinol ligand the breakthrough of ethylene occurred sooner than it had with pyridine, possibly indicating a slower uptake rate, but possibly due to greater hydrophilicity of the ligand solution which might inhibit gas/liquid contact. Of the other ligands tested, only 4-picoline had appreciable uptake, registering 27 cc/cc in one trial, but lower values in the other tests. This ligand is more hydrophobic than pyridine so it is expected to give worse olefin selectivity. The Me5-dien ligand results could not be reproduced, with only 1 cc/cc on a second trial.

Table 1. Effect of Ligand on Ethylene Uptake for 2 M Cu, L/Cu = 2 Facilitators in Batch Experiments

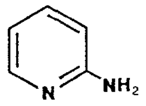
Ligand	bp (or mp) C	Ethylene capacity cc C2= / cc solution	C2= Breakthrough mins
Pyridine	115	28	30
Imidazole	256	6	0
Niacin	mp 236-238	9	0
2-aminopyridine	207	0.3	0
3-pyridylcarbinol	266	28	10
Me5-dien	198	*18	0
Niacinamide	mp 128-131	0.2	0
2-picoline	128	0.1	0
3-picoline	144	2	0
4-picoline	145	*15	15
4-hydroxypyridine	230-235	6	0
3-hydroxypyridine	mp 126-128	4	0
2-hydroxypyridine	280	0	0

* Capacity measurements were widely scattered.

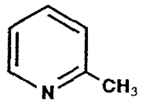
PYRIDINE 1°
C.A. 9 CI Name: Pyridine



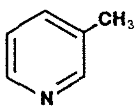
2-AMINOPYRIDINE
C.A. 9 CI Name: 2-Pyridinamine



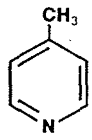
ALPHA PICOLINE
(2-Picoline)
C.A. 9 CI Name: Pyridine, 2-methyl-



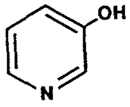
BETA PICOLINE
(3-Picoline)
C.A. 9 CI Name: Pyridine, 3-methyl-



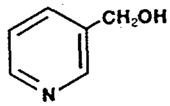
GAMMA PICOLINE
(4-Picoline)
C.A. 9 CI Name: Pyridine, 4-methyl-



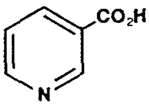
3-HYDROXYPYRIDINE
C.A. 9 CI Name: 3-Pyridinol



3-PYRIDYL CARBINOL
C.A. 9 CI Name: 3-Pyridinemethanol



NIACIN U.S.P. GRANULAR
(Nicotinic Acid)
C.A. 9 CI Name: 3-Pyridinecarboxylic acid



NIACINAMIDE, FEED GRADE
(Nicotinamide, feed grade)
C.A. 9CI Name: 3-Pyridinecarboxamide

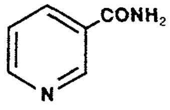


Figure 3. Ligands Tested as Substitutes for Pyridine in 2M Cu Facilitator Solutions

Optimization of the py/Cu ratio and Cu(I) concentration

An attempt was made to optimize the solution capacity as a function of the py/Cu(I) ratio for the base 2 M Cu facilitator solution. Solutions were prepared with py/Cu ratios from 2.1 to 3.0 and their ethylene uptakes measured for several cycles. The data are presented in Figure 4. The conclusion from this study was that a py/Cu ratio of about 2.1-2.3 was optimal, although lower ratios should be examined. As shown in the Figure neither a linear nor a cubic function fit the data very well.

Ethylene uptake was also measured as a function of the concentration of Cu for solutions with py/Cu ratios of 2. As the concentration of metal was increased from 0 to 4 M the uptake of ethylene increased linearly, as shown in Figure 5. The broken line in Figure 5 represents one ethylene absorbed per Cu atom in solution. The best fit to the absorption data indicates that about 48 % of the Cu atoms are complexed with ethylene for all concentrations at 23 C and 1 atm ethylene pressure. This indicates that there is little interaction between Cu complexes of a cooperative or inhibitive nature and represents a single vapor liquid equilibrium (VLE) point.

Ethylene Uptake Rates

Ethylene uptake was measured by admitting ethylene to solutions of the Cu facilitators and measuring the gas volume that exited the solution. The uptake is expressed as the amount of ethylene absorbed in the solution as a function of time. Data for several facilitator solutions is presented in Figure 6. For all of these facilitator solutions it is clear that the rate of ethylene uptake is equal to the rate of ethylene admission for most Cu-ligand complexes for 20 minutes or more, until they reached saturation. The saturation amount represents the capacity. Not much can be said about differences among the ligands from these measurements since all of the facilitators absorb relatively rapidly.

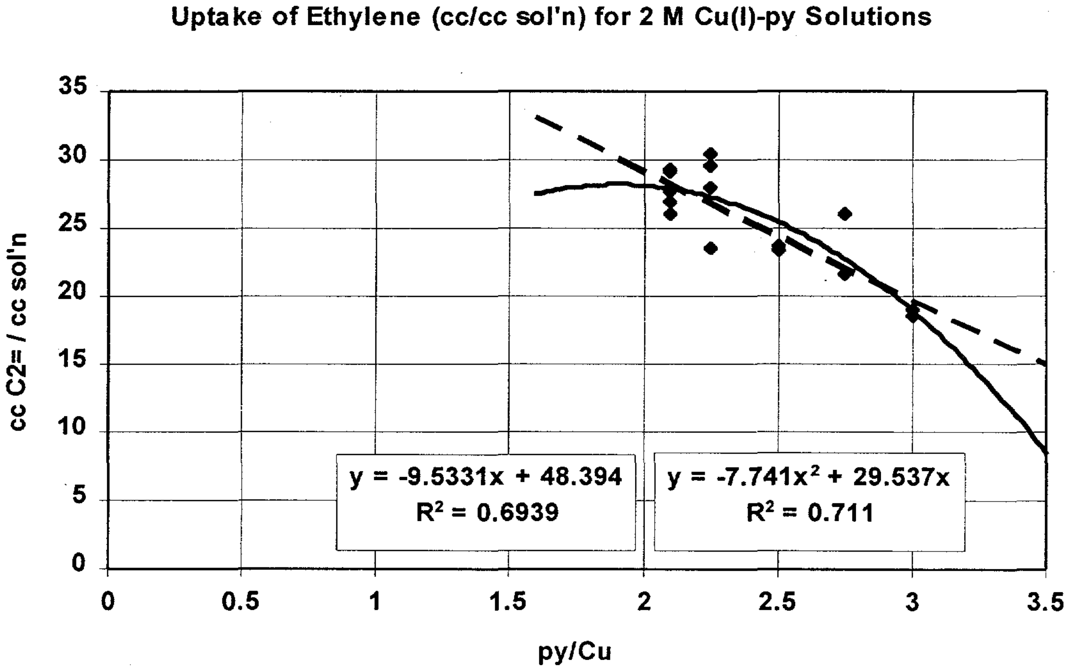


Figure 4. Ethylene uptakes measured as a function of py/Cu ratio for 2M Cu solutions

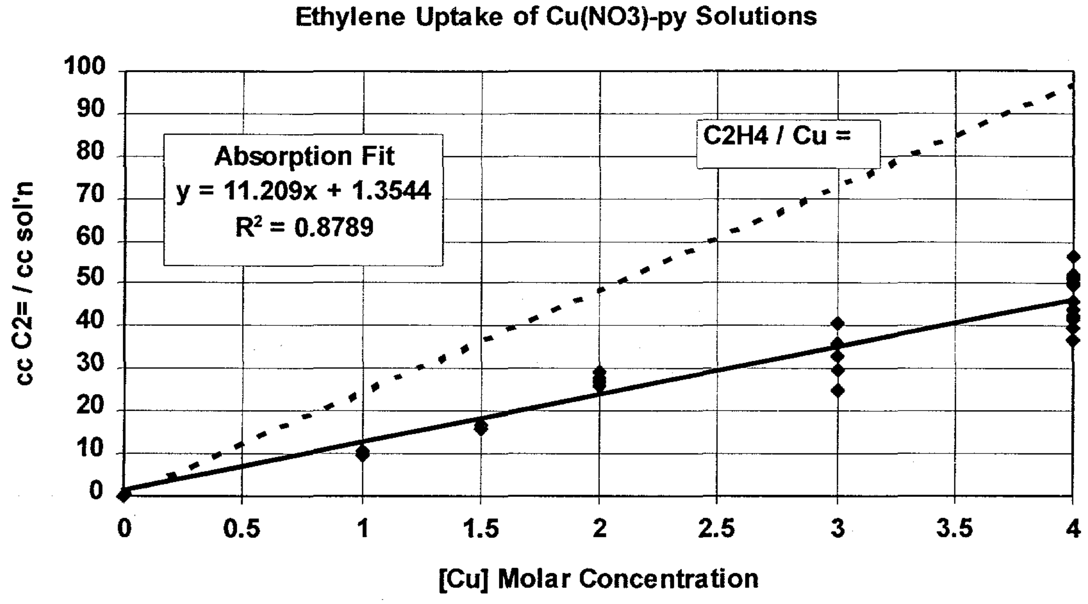


Figure 5. Ethylene uptakes measured as a function of Cu concentration for py/Cu=2.

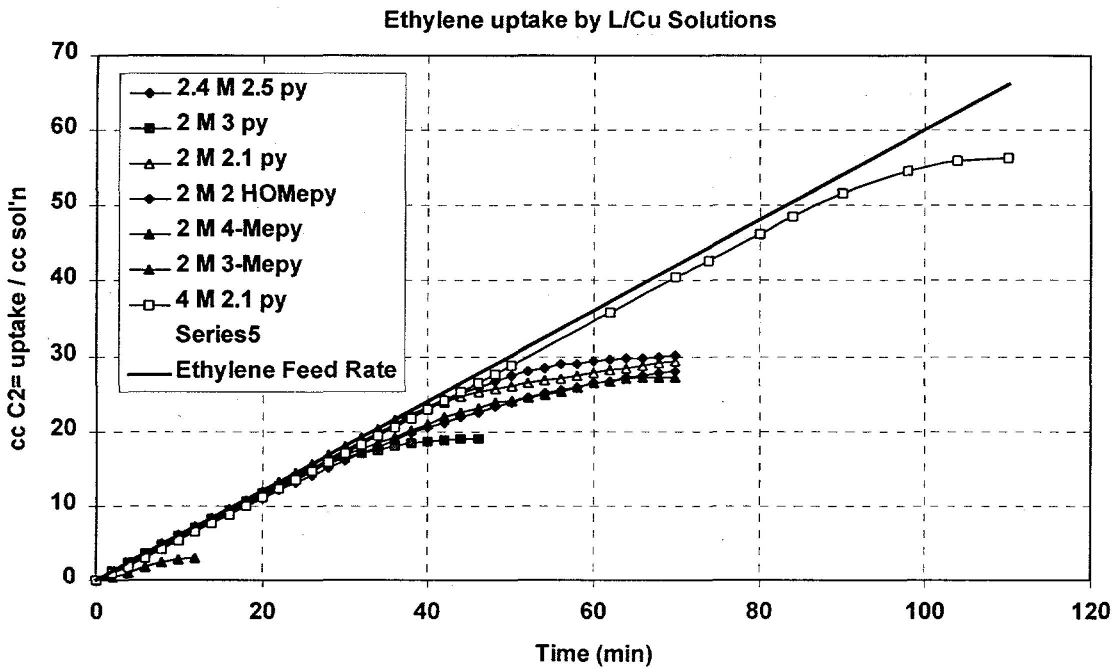


Figure 6. Ethylene Uptake Rates for L/Cu Facilitator Solutions.

Suppressing Formation of Red-Orange Solid

Valus noted that use of Cu(I) solutions prepared from Cu(II) and Cu(0) always left a solution that was "heterogeneous, indicating either incomplete conversion to Cu(I) or formation of some degradation products." No efforts were made to identify the solids or prevent their formation.

Repeated or prolonged heating of any of the Cu(I)-ligand solutions resulted in formation of a red-orange solid, not visibly differentiable from the Cu(0) powder used in the solution preparation. Analysis of the solids freshly removed from the solution by IR shows some nitrate ion and pyridine (Figure 7), but after two weeks exposure to air the material consisted only of CuO and Cu_2O. X-ray diffraction confirms the identification of the aged solids as a mixture of copper oxides (Figure 8). When the solids were washed with HNO3 before collection there was little change in the IR and only a trace of Cu(0) appeared with the oxides in the XRD. We concluded that the solids are primarily Cu_2O contaminated with some adventitious Cu(I)-pyridine nitrate salt. **It became a critical objective to minimize the red-orange solid formation** since it could make the process unworkable on a commercial scale. We postulated that the Cu_2O formed by dehydration of an intermediate Cu(I) hydroxide formed by hydrolysis. Furthermore we postulated that by inhibition of Cu(I)-OH formation we could inhibit solids formation.

In order to test for solution stability against oxide formation, facilitator solutions were prepared and heated to 80 C overnight, or longer. Addition of excess cupric ion was tested as a means of inhibiting hydroxide formation, as reported in one patent[i], but without success. Excess nitrate in the form of $NaNO_3$ was tested for the 'common ion effect' to limit hydroxide formation, but solids were still observed with either pyridine or the best pyridine substitute, 3-pyridylcarbinol. 1,4 dioxane was tested as solvent but although capacity remained 25 cc/cc solids were formed. A solution of Cu(I) in propionitrile, in which propionitrile was expected to act as both solvent and ligand had a capacity of only 1 cc/cc.

Acidification of the facilitator was postulated to prevent hydroxide formation by minimizing the concentration of hydroxide ion. The first experiment with HNO3 added to the 2 M, py/Cu 2/1 facilitator resulted in capacity reduction to 11 cc/cc but solids formed slowly. It was thought that the HNO_3 could be protonating the pyridine, thus reducing the effective L/Cu ratio below 2 and changing the capacity as well as permitting hydroxide formation. Thus an experiment was run using an excess of pyridine along with the added HNO_3. The assumption was that the pyridinium nitrate formed would buffer the solution without reducing the effective pyridine concentration, as in Equation 1.

$$\mathbf{HNO_3 + pyridine \Rightarrow [Hpy]^+NO_3^- \quad (1)}$$

Addition of HNO_3 effectively inhibits formation of Cu_2O, as shown in Table 2, when used with excess pyridine, without significantly reducing absorption capacity. Solutions of the Cu(I)-pyridine-HNO_3 formulation have been heated to 80 C for more than 300 hours under N2 without formation of any solids.

Table 2. Capacity Measurements and Solids Formation with HNO3 Adicified Cu(I) Facilitator Solutions.

Ligand with 2 M $CuNO_3$	HNO_3	Capacity, cc/cc *	Min to Ethylene Breakthrough	Solids
2 py	2 M	11	6	slow
2.5 py	2 M	19	22	no
3 py	2 M	16	6	no
2.75 py	2 M	22	35	no
2.75 py	3 M	22	30	no

* These values are corrected from those reported in the Appendix to account for the increased solution volume due to HNO3 addition.

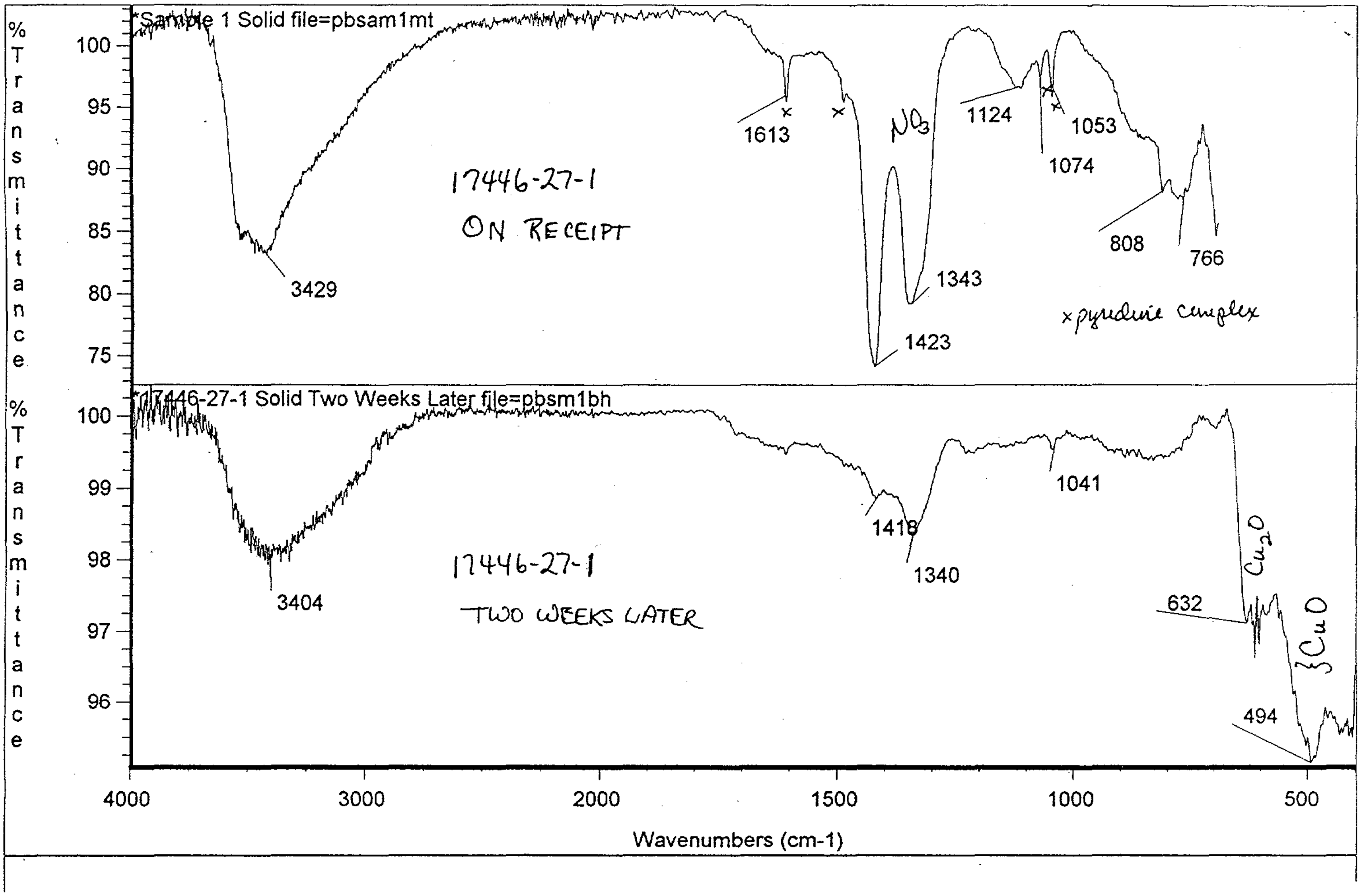


Figure 7 **Infrared Spectra of Solids Recovered from Cu(I) Facilitator Solution (a) Fresh and (b) Two Weeks Later**

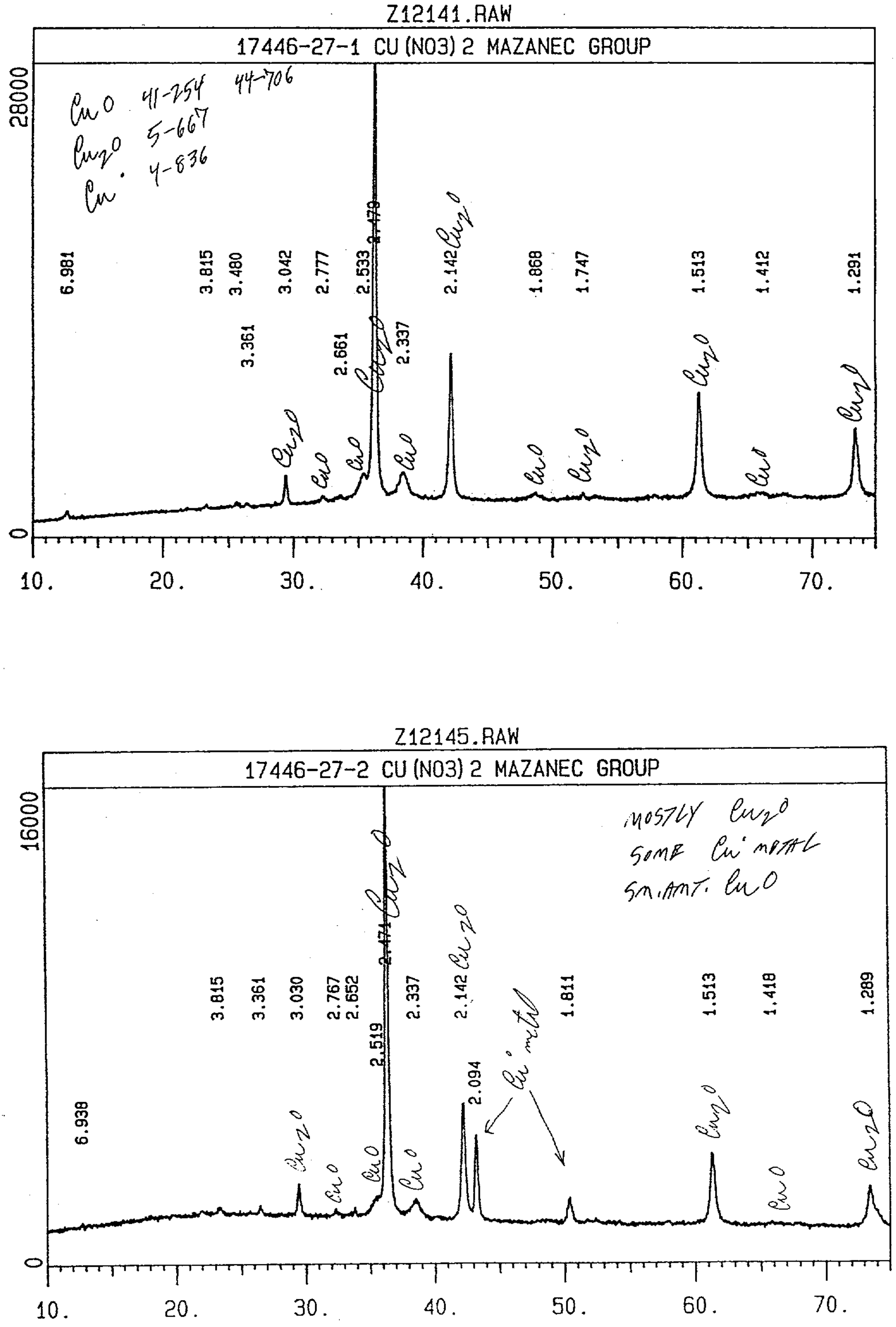


Figure 8 XRD Patterns of Solids Recovered from Cu(I) Facilitator Solution (a) Fresh and (b) Two Weeks Later

Upon cooling the lean solutions of 2 M Cu(I)-pyridine-HNO_3 1/2.75/1 solidification was observed. This was not the irreversible formation of copper oxide, but rather the crystallization of the Cu-py complex. The solid was found to redissolve at about 35-40 C, so gentle heating could prohibit its formation. Furthermore, admission of ethylene caused the solid to redissolve as well. A quick test to determine the minimum ethylene pressure needed to redissolve the solid showed that when a gas mix of 15-20 % ethylene in He (0.15-0.20 atm ethylene) was passed through the solution at 25 C all the solids dissolved.

Continuous Demonstration of the Absorber/Stripper Process

Capacities and stabilities can be measured in batch reactions, but the commercial process requires continuous circulation of the facilitator solution. A simple reactor was set up to measure ethylene recoveries and selectivities in a continuous mode, as shown in Figure 2. The reactor can handle up to about 300 cc of facilitator solution and separate up to 100 sccm of ethylene.

In the first experiments, with a recycle pump rate of some 60 sccm, steady removal of 90+ % of a 50 sccm feed of ethylene was measured. Separation of ethylene from nitrogen and ethane was demonstrated, as was the recovery of propylene. Ethane concentrations detected in the product stream were very low indicating the olefin/paraffin separation ratio is very high. The first test ran some 200 hours with stripper bath temperatures as high as 100 C without the formation of solids, confirming the stability of the solution demonstrated in batch reactions. This is the first confirmation of the absorber/stripper concept with an aqueous Cu-based facilitator.

Table 3 presents the results of further experiments on selectivity using the 2 M Cu(I)-pyridine-HNO_3 1/2.75/1 facilitator. Since the absorber column was only 30-50 cm in height (depending on the liquid leveling device), the system can be expected to yield either high selectivity or high recovery, but not both at the same time. The stripper is only a round bottom flask, so poor gas-liquid separation is expected. Nevertheless, the results in Table 3 show that recoveries of ethylene can be high and selectivities for ethylene are good. Importantly it is observed that as the gas feed rate is raised the selectivity of ethylene increased significantly. Higher gas/liquid flow ratios are needed to demonstrate the 1000-2000 ethylene/ethane selectivity ratio needed for high purity ethylene production.

Table 3. Results for Continuous Ethylene Separation Using a 2 M Cu(I)-pyridine-HNO_3 1/2.75/1 Facilitator; Liquid Recirculation Rate ~ 75 sccm

Feed	Gas Feed Rate, sccm	Ethylene Recovery %	$C2^=/C2$ Selectivity Ratio	Stripper Bath Temp C	Stripper Pot Temp C
$C2^=$	52	23	-	82	-
$C2^=$	73	27	-	112	76
$C2^=$	146	45	-	112	78
$C2^=$	70	83	-	-	49
$C2^=$	140	64	-	-	63
$C2^=/C2$ 50/50	67	69	98	78	-
$C2^=/C2$ 50/50	67	57	49	-	50
$C2^=/C2$ 50/50	100	99	75	-	61
$C2^=/C2$ 50/50	200	60	101	-	57