

**Optimization and Scale Up of a Silicate
Precursor to Ceramics**

By

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Thesis

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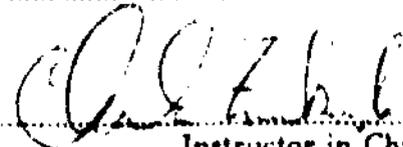
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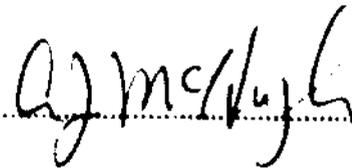
ENTITLED: Optimization and Scale Up of a Silicate Precursor to Ceramics

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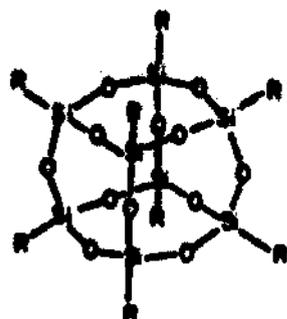
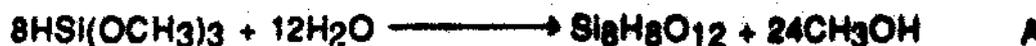
HEAD OF DEPARTMENT OF Chemical Engineering

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INTRODUCTION

The acid catalyzed hydrolysis and condensation of silicon acid esters yields octasilsesquioxane¹ (see Figure 1), commonly referred to as the "cube", as shown in A.



!



As precursors for ceramics, a number of products ranging from highly porous aerogels², to thin films and optical-quality glass fibers³, to dense monolithic glasses⁴ may be prepared depending on processing conditions. Polymerization of this cube monomer can introduce interesting properties in car engine blocks or tiles due to its structural rigidity. Unfortunately, emulsions during the washing step of the synthesis limit the yield of Si₈H₈O₁₂ to 8%. The yield is further constrained because much of the starting material is converted to polymers, which are thermodynamically favored since they are more disordered, and less energy is needed to create them.

The objective of this Senior Thesis was to optimize the yield of octasilsesquioxane and to design a reactor and product separation and purification equipment for its production. Significant quantities of these particles of uniform size and shape are needed for Professor Zukoski's research. Thus, design specifications were based on a four-fold scale-up of synthesis A (see Experimental).

OPTIMIZATION

EXPERIMENTAL

Reagents, Solvents, and General Procedures. Trimethoxysilane (Petrarch Systems) was distilled under nitrogen prior to use. Cyclohexane (Fischer), concentrated HCl (Malinckrodt), and glacial acetic acid (Malinckrodt) were used as received. HCl gas (Air Products) was dispensed from small pressure tanks. All experiments were made inside a fume hood. Cyclohexane was recycled by refluxing at 80 C and storing over CaCl₂ pellets. The pellets were activated by drying at 250 C for 24hrs. and storing under nitrogen at room temperature.

A. Preparation of $\text{Si}_8\text{H}_8\text{O}_{12}$. A 12L three-neck flask with overhead stirrer and 1L pressure-equalizing addition funnel with metered stopcock was charged with 1.125L glacial acetic acid and saturated with HCl by bubbling the gas through the liquid for 15 minutes. To this mixture, 1.5L cyclohexane and 40ml concentrated HCl were added. A solution of 122g (1.0mol) $\text{HSi}(\text{OCH}_3)_3$ and 1.5L cyclohexane was placed in the funnel and added to the reaction mixture at ca. 275ml per hour. At the end of addition, the mixture was stirred an extra 30 minutes and then transferred in 1L quantities to a 2L separatory funnel to remove the acid phase. Each organic layer was washed with $3 \times 0.75\text{L}$ water (ca. 60 C), which formed creamy white emulsions, to pH=4.5. The cyclohexane was immediately removed on a rotary evaporator at 40 C and the resulting tacky, white solid was dried under vacuum overnight. The material was crushed to a fine powder and extracted with 1L boiling cyclohexane. After the hot mixture was vacuum filtered through glass wool, the cyclohexane was removed by simple distillation until the solution volume was about 250ml. Colorless crystals were produced upon cooling to room temperature. These were collected by decanting the solution and dried under vacuum overnight. The volume of the mother liquor was then reduced to about 100ml by boiling off the solvent. Upon cooling to room temperature, more crystals were produced. This procedure was repeated once more, and all crude material was purified by sublimation (130 C, 0.5 torr). A total of 3.80g (8.95mmol, 7.2% yield) of white $\text{Si}_8\text{H}_8\text{O}_{12}$ crystals were obtained.

B. Preparation of $\text{Si}_8\text{H}_8\text{O}_{12}$ (1/6 scale). A 2L three-neck flask with overhead stirrer and 1L pressure-equalizing addition funnel with metered stopcock was charged with 187ml glacial acetic acid and saturated with HCl by bubbling the gas through the liquid for 5 minutes. To this mixture, 250ml cyclohexane and 6.67ml concentrated HCl were added. A solution of 22.3g (0.167mmol) $\text{HSi}(\text{OCH}_3)_3$ and 250ml cyclohexane was placed in the funnel and added to the reaction mixture at ca. 275ml per hour. At the end of addition, the mixture was stirred an extra 15 minutes and then transferred to a 1L separatory funnel to remove the acid phase. The organic layer was washed with $3 \times 200\text{ml}$ water (ca. 60 C), which formed creamy white emulsions, to pH=4.5. The cyclohexane was immediately removed on a rotary evaporator at 40 C and the resulting tacky, white solid was dried under vacuum overnight. The material was crushed to a fine powder and extracted with 250ml boiling cyclohexane. After the hot mixture was vacuum filtered through glass wool, the cyclohexane was removed by simple distillation until the solution volume was about 100ml. Colorless crystals were produced upon cooling to room temperature. These were obtained by decanting the solution and dried under vacuum overnight. The volume of the mother liquor was concentrated down to 25ml by boiling off the solvent. More shiny crystals were produced upon cooling to room temperature. The remainder of

the solution was attached to a liquid nitrogen cold trap and put under vacuum overnight. White, clumpy material was produced, which was sublimed with the crystals to reveal 0.1561g (0.368mmol, 1.5% yield) of $\text{Si}_8\text{H}_8\text{O}_{12}$.

Synthesis B(1/6 scale) was followed verbatim (i.e., equipment, operating conditions, volumes) for the experiments listed below except for the listed changes.

C. The volume of concentrated HCl was changed; 3.33ml was added to the reaction mixture. A total of 0.2643g (0.622mmol, 2.7% yield) of $\text{Si}_8\text{H}_8\text{O}_{12}$ was obtained.

D. The volume of concentrated HCl was changed; 1.67ml was added to the reaction mixture. A total of 0.2637g (0.621mmol, 2.7% yield) of $\text{Si}_8\text{H}_8\text{O}_{12}$ was obtained.

E. To break emulsion in the washing step, both phases were centrifuged for 15 minutes at 500RPM. A white, crusty film surrounded the sides of the plastic bottles upon completion of the spinning. The phases were put back into the separatory funnel to discard the aqueous layer. Another 200ml of water was added to the reaction mixture and the two phases were centrifuged again. Thus, this washing, centrifuging, discarding procedure was repeated for a total of 4 times. Boiling cyclohexane was added to the white, crusty material. However, after filtration and cyclohexane distillation, crystals did not come out of solution. Synthesis B continued on the centrifuged organic layer and a total of 0.3219g (0.758mmol, 3.4% yield) of $\text{Si}_8\text{H}_8\text{O}_{12}$ was obtained.

F. After the addition of trimethoxysilane solution was complete, half of the mother liquor was stored in a refrigerator at 5 C while the rest was left standing at 25 C for 24hrs. The batch that was "put in the cold", so as to concentrate it, did not form crystals. Likewise, crystals were not produced from the room temperature batch when Synthesis B was continued.

DISCUSSION

My attempt to optimize reaction A was a venture into "black magic", for although much work had been previously conducted by Frye and Millar⁵, their efforts to increase yield were fruitless. For example, Millar obtained a 3% yield (1.50g, 3.53mmol). However, I was to conduct further research on the reaction on a 1/6 scale. This scale used used so as to minimize the cost of starting materials. Discovering the reaction's limitations would thus affect the degree

of scale-up. My goal was to achieve reproducible yields and then to optimize the reaction by varying certain parameters in its preparation.

A number of techniques were learned/discovered that increased the yield to 8%. Lukewarm water (ca. 60 C) was used in the washing because the degree of emulsification was less than with tap water or boiling water. The washing itself was done in slow, rhythmic, back and forth movements since violent, aggressive jerks tended to increase emulsification. When the tacky, white solid was extracted with boiling cyclohexane, the solution was stirred in an oil bath for 10 minutes at 80 C before filtration. This ensured that as much cube as possible dissolved.

The yield of synthesis B was 1.5%, indicating that scaling down or up will effect yields due to changes in concentration or velocity profiles. Scaling is an extrapolation into the unknown which, as evidenced by syntheses A & B, will not necessarily give linear similitude in yield. When the volume of concentrated acid was decreased (syntheses C & D), the yield increased to 2.7%. One explanation is that a smaller acid (water) amount decreases $\text{HSi}(\text{OCH}_3)_3$ polymerization. (Trimethoxysilane readily forms long silicon chains upon prolonged exposure to moisture.). However, the yields were identical because the difference in volume (3.33ml vs. 1.67ml) was already so small that these amounts could have been the minimum to sustain reaction A. A more noteworthy result was obtained from synthesis E, where centrifugation was used to destabilize the emulsion so as to recover some of the cyclohexane. The yield increased to 3.4%. The solution's volume was about 100ml greater after washing/centrifugation than after just the washing. Finally, synthesis F showed that if the reaction mixture was not immediately washed (within 1 hour), then the tremendous excess of acid would decay or degrade the cube. This proved that the cube is formed in the addition, not in the washing step. This also indicated that the scale-up could not be too big or else there would not be enough time to complete the first stage of the synthesis (addition/washing/evaporation) in one day

SCALE UP

ISSUES

Scale-up of the cube focused on the following considerations: equipment specifications, materials of construction, equipment installation, and safety.

Equipment design involved calculating size in terms of volume. What unit operations were required in the flow diagram that equipment had to be designed for? Would the equipment be purchased, or fabricated at RAL machine shop? Would it be modeled after laboratory glassware? What modifications were necessary to accomodate auxiliary components such as

valves and stirrer? For example, how would the trimethoxysilane solution be added to the reaction mixture? A four-fold preparation would call for a total of 6.5L of $\text{HSi}(\text{OCH}_3)_3$ and cyclohexane. But, due to the hood's limited size, it could not be gravity fed from a 7L addition unit. The solution could be mechanically pumped in but nonreactive feed lines would be needed. A hand pump labor intensive and impractical.

Physical properties of constructional material were important factors in design of the equipment. The material had to possess structural strength and resistance to physical shock and to corrosive chemicals. Furthermore, it had to be inexpensive, lightweight, and shatterproof.

Equipment had to be mounted on a wooden table in a walk-in fume hood for immobilization. Could UNI-STRUT be attached to the hood's liner to support the equipment? Would the equipment be glued, bolted, or tied down? How would the table be modified?

Finally, health and safety hazards were addressed. Though performed in a well ventilated fume hood, the synthesis involved dangerous solvents. Trimethoxysilane is corrosive, flammable, and very toxic; it is a deadly eye and skin irritant. Acetic acid and hydrochloric acid are both corrosive liquids. Cyclohexane has a very low flash point (-1 F). Its vapors form explosive mixtures with air that may be set off by a motor's spark. Ignition sources such as open flames, sparks, and heated materials had to be eliminated. Storage, fire-fighting materials, and threshold limits were other characteristics that had to be known about the solvents. These issues would then be incorporated into the type of protection needed by handlers.

DESIGN

A four-fold scale-up of the cube required a reactor and scrubber. Reaction A continuously emits HCl, acetic acid, and silicate gases and vapors which must be vented but cannot be disposed of directly into the hood for fear of corrosion. Therefore, the gases had to be dissolved in a contacting liquid.

The most difficult aspect of the design was creating an agitation system for the reactor. A metal shaft, like Type 316 stainless steel, could not be used because the acids would "eat" it away. A glass or plastic shaft had to be wide enough and have a propellor long enough to promote turbulent mixing. The shaft also had to be rigid since it was going to operate at high torque and high RPM. Furthermore, a mounting was necessary for the reactor lid in which to insert the shaft and give it support.

A pressure difference will transport the trimethoxysilane solution, placed under nitrogen in a 10L, polyethylene Nalgene carboy (Fischer), through Teflon tubing to a reactor at atmospheric pressure. The tubing will be connected to a 0.5" O.D. plastic pipe adapter on the top side a 50L, polyethylene Nalgene carboy-reactor (Fischer). RTV silicone rubber will be used

for sealings. An 8" Teflon jacket will be fastened to the carboy's lid with 4 Nylon screws. Through this sleeve, a Teflon coated, stainless steel shaft and paddle (Ace Glassware) will be inserted. A pipe adapter on the other side of the reactor will serve as a vent to a 6" O.D. Plexiglass scrubber. For good liquid distribution, water will enter through two adapters and a perforated lid for, and come in countercurrent contact with HCl and other vapors in a layer of 0.50" ceramic Intalox saddles. The ratio of individual packing diameter to tower diameter, 1:12, discourages channeling. Industrial operations recommend a ratio of 1:15. The scrubbed solution will then exit through a bar grid-shaped packing support into a sink at the side of the hood. Gases will pass from the reactor via Teflon tubing to a pipe adapter at the bottom side of the scrubber. Threads will be drilled into the Plexiglass shell to accommodate the adapters. Teflon tape will be used for sealing. Polypropylene trays (Baxter), 20"x20"x6" and 12.75"x10.25"x4.25", will contain possible leaks from the reactor and addition tank. Spigots, attached to both trays, will remove any "spills" to waste solvent containers. A tube from the reactor's spigot will pass through a hole drilled at the top of the reactor tray to remove extraction by-products to waste containers. Unfortunately, the hood liner was determined too brittle for UNI-STRUT by its manufacturer (Hamilton). The reactor and tank will be situated between four, 1' high aluminum bars. Holes will also be drilled to half the table's width for a tight press-fit of the scrubber's legs. The mixer will be clamped to an iron bar framework.

OPERATION

The extraction requires two stages, 10L and 7L of water respectively. As seen in the enclosed phase diagram⁶, the first washing will produce 33 mass% $\text{CH}_3\text{CO}_2\text{H}$ in the extract while the second washing will reduce it to 0.58 mass% $\text{CH}_3\text{CO}_2\text{H}$, corresponding to pH=4.5. Because pH of the extract is measured, the raffinate is neutralized when the extract has around 0-1 mass% of acid. This is a good design for two reasons. One stage with 22L of water would give an extract that contains 18 mass% $\text{CH}_3\text{CO}_2\text{H}$. A larger volume of solvent could not be used because the reactor only has a 50L capacity, 16L of which already holds the acetic acid and cyclohexane. Second, a three stage process would increase the interfacial area, causing more emulsions.

Cyclohexane will be removed on a Yamoto RE-51 continuous feed rotovapor. A hose, connected to the unit's glass nipple, is placed in the solvent pot. Opening a stopcock slowly draws fluid into the nipple and through a 8" glass tube insertion that leads to the evaporating flask, where the fluid drips in. Thus, the process runs on a continuous basis and is intended for evaporation of large quantities of solvent (greater than 2L).

The extraction of acetic acid produces a large amount of emulsions. For cleaning, the reactor and its connecting tubes will be periodically flushed with water. The extraction will also produce ca. 25L of waste that can not be dumped in sinks. It will be put in plastic waste containers and picked up by the University. Finally, recycled cyclohexane (see Experimental) can not be used in the extraction of the tacky, white solid because it may contain lingering acid. However, it can be used in the addition step.

A discussion with Amy Daniel (333-2755) of the Division of Environmental Health and Safety resulted in the following safety advice. Operators should wear goggles, chemically resistant gloves, and a respirator when handling solvents. No more than six gallons of class A liquids such as cyclohexane can be stored in the solvent cabinets of 164 Davenport Hall. An explosion-proof, totally enclosed motor should be purchased to prevent detonation of cyclohexane vapors.

RECOMMENDATIONS

1. Obtain NMR of reaction mixture to determine at what point the cube is formed.
2. Change other variables in synthesis A to see if the yield can be increased beyond 8%:
 - a. Use centrifugation
 - b. Use a smaller volume of concentrated HCl
 - c. Use centrifugation and a smaller volume of concentrated HCl.
 - d. Replace current semi-batch runs with batch runs.
3. Obtain HCl/water equilibrium data to calculate required packing depth of scrubber.

CONCLUSIONS

1. On a 1/8 scale, the yield of $\text{Si}_2\text{H}_3\text{O}_{12}$ was increased by using centrifugation and less acid.
2. On a full scale, reproducible yields of 8% were achieved.
3. A four fold scale-up of synthesis A will not necessarily result in a four fold increase in yield unless the following is done:
 - a. Dimensional analysis on fluid correlations.
 - b. More experiments with as wide a range of variables as possible.
4. A four-fold scale-up will cost about \$1250.
5. Most importantly, design work requires an understanding of engineering sciences and the ability to apply this knowledge to practical situations.

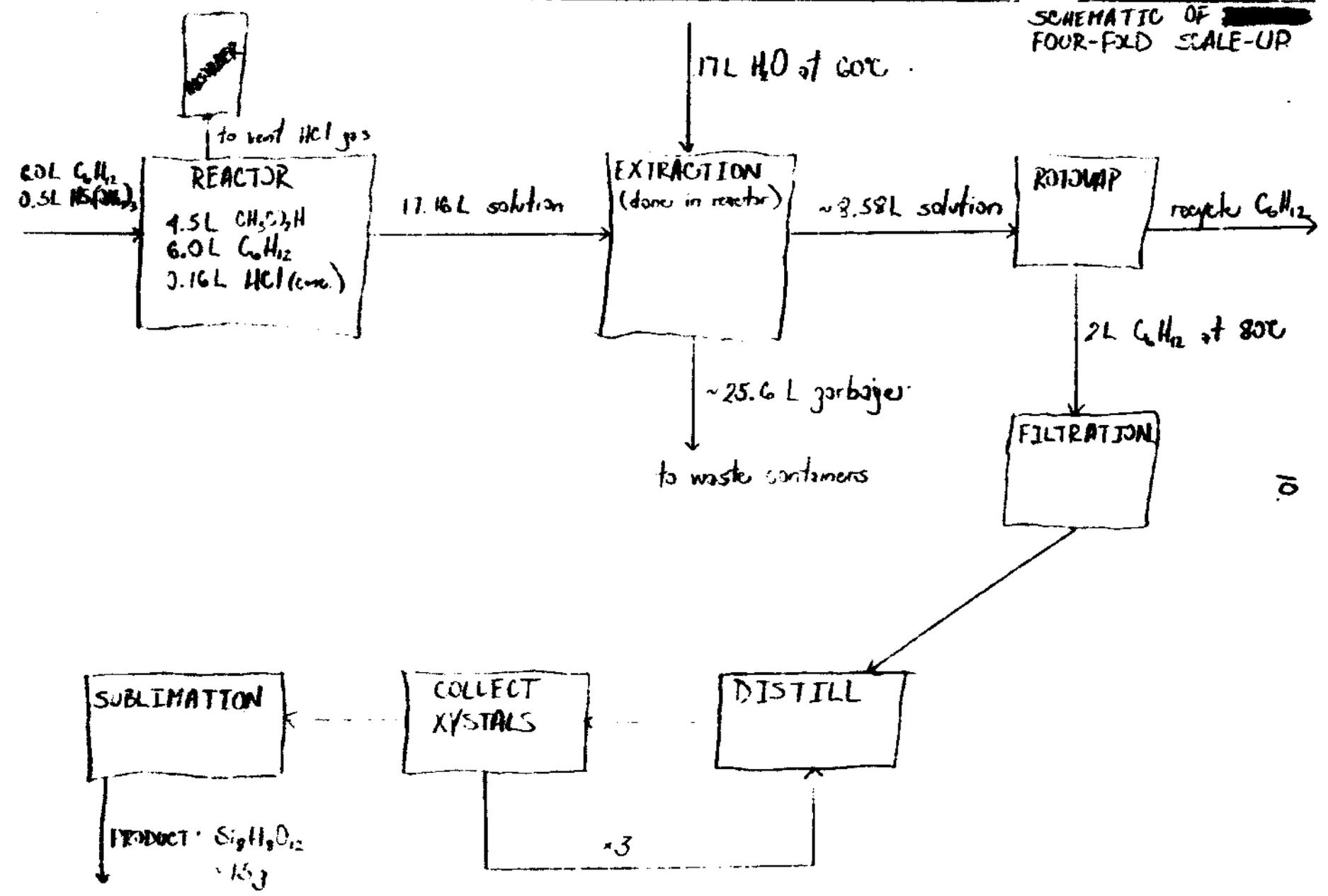
ACKNOWLEDGEMENTS

I thank Walter Klemperer and Chip Zukoski for support of this research. Both professors provided invaluable technical assistance.

REFERENCES

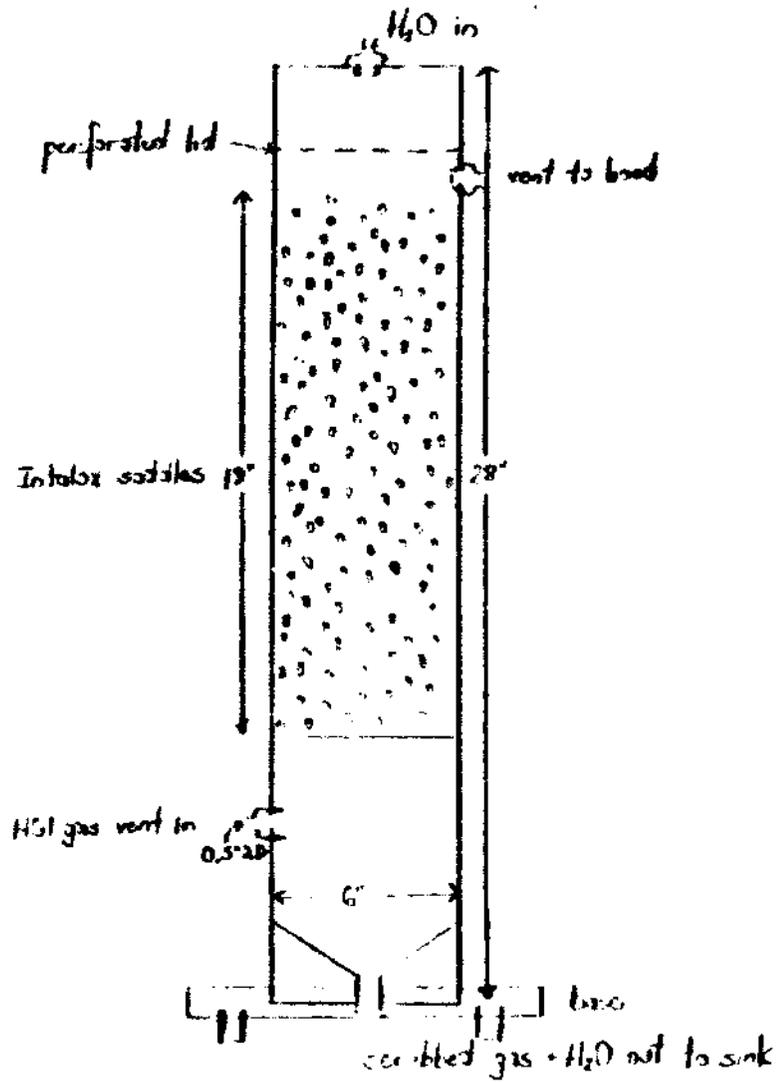
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SCHEMATIC OF ~~REACTOR~~
FOUR-FOLD SCALE-UP

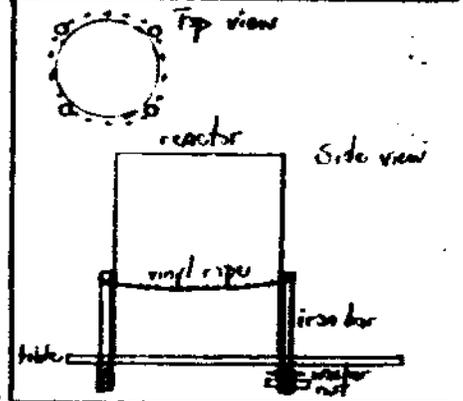
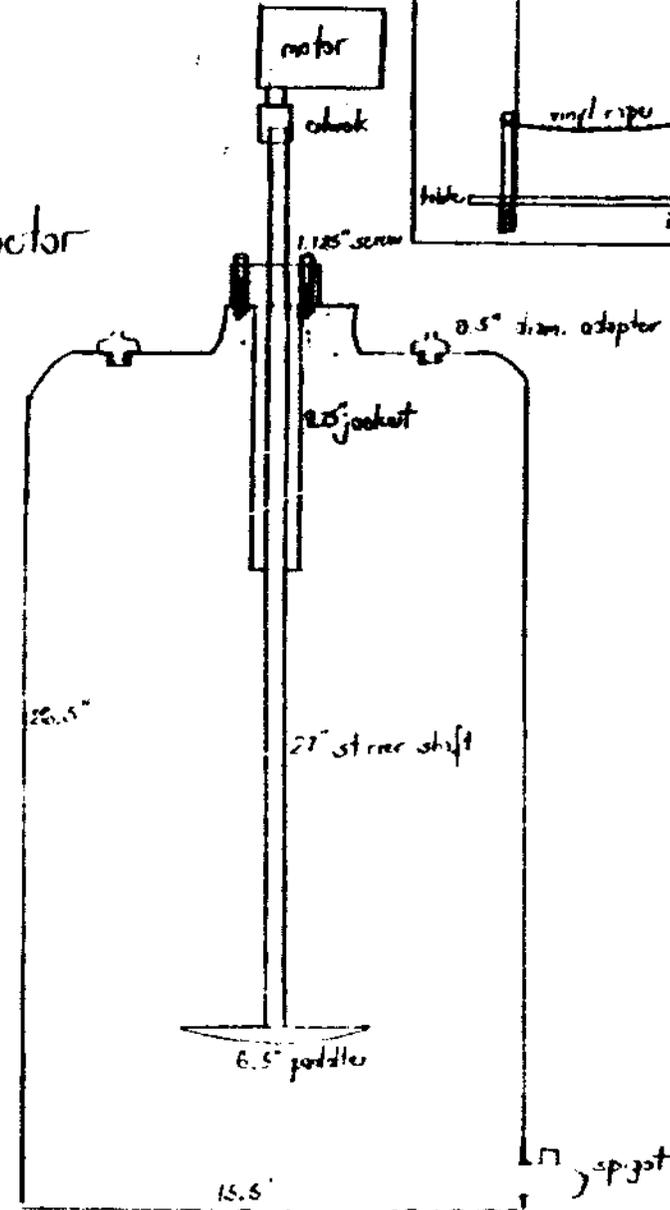


EQUIPMENT DESIGN

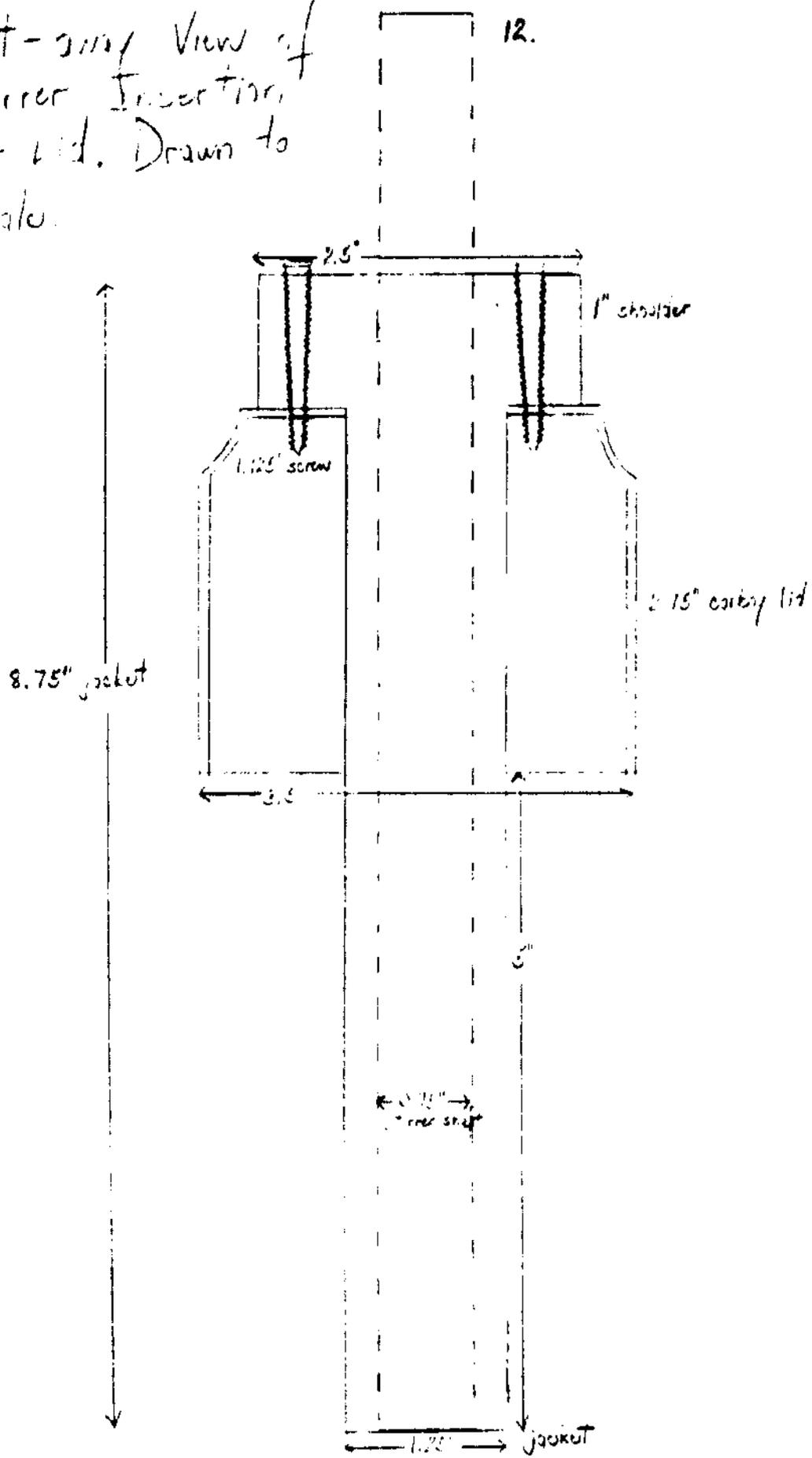
Scrubber

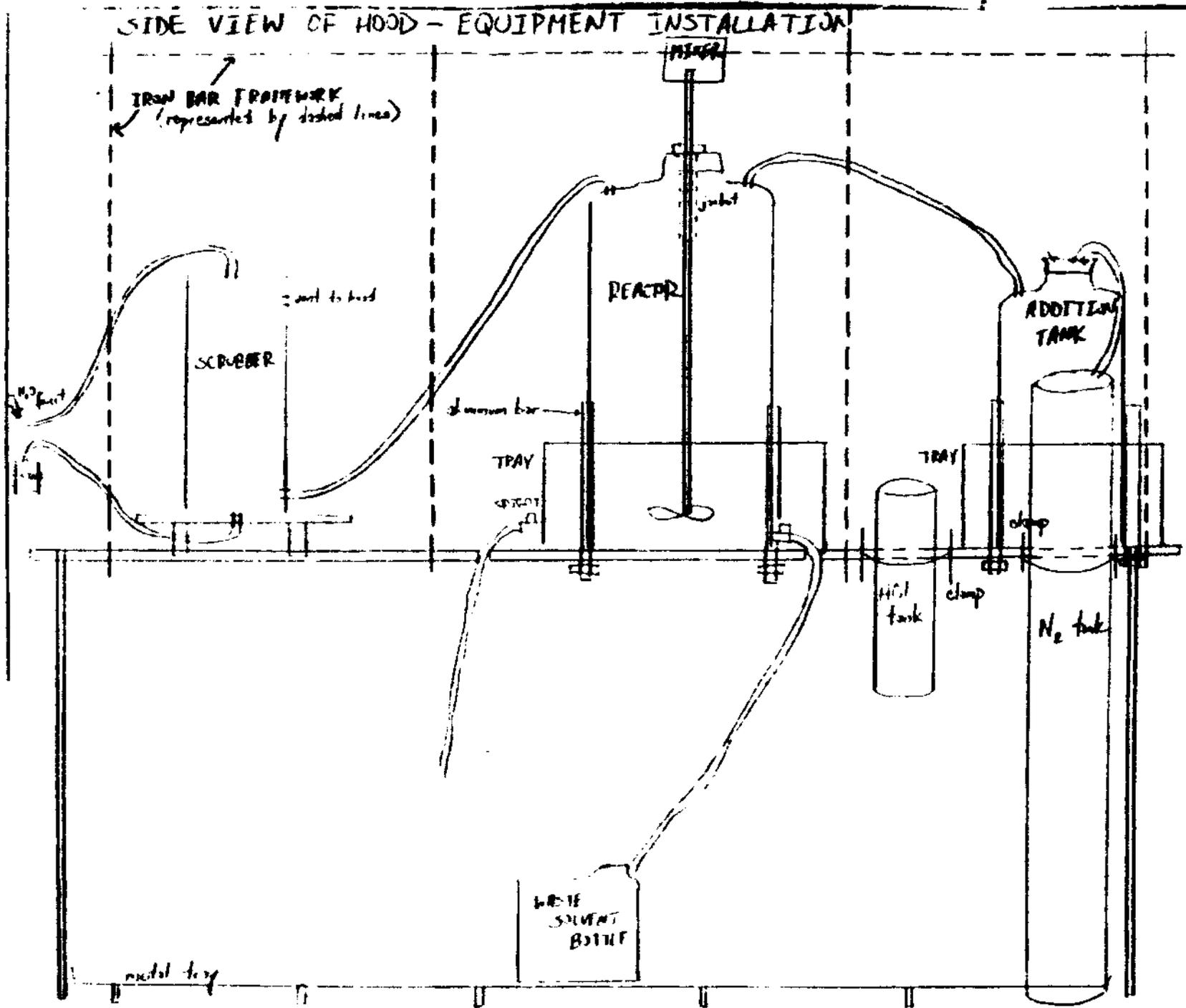


Reactor



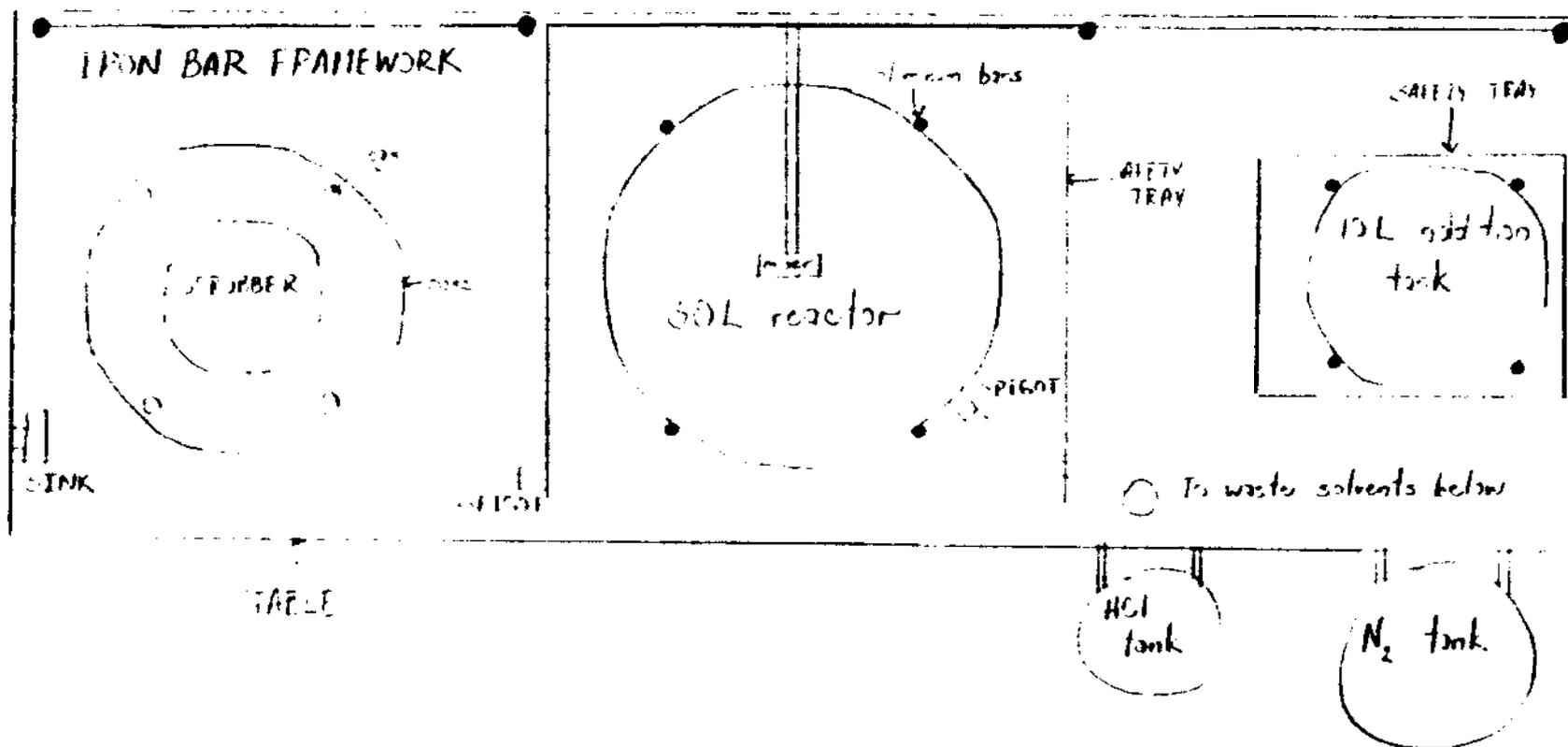
Bot-view of
Stirrer Insertion,
is- lid. Drawn to
Scale.





TOP VIEW OF HOOD - EQUIPMENT INSTALLATION

SCALE 1in : 6in



EXTRACTION CALCULATIONS 15.

Acetic Acid : $1.051 \text{ g/ml} \times \frac{1000 \text{ ml}}{\text{L}} \times 4.5 \text{ L} = 4729.5 \text{ g}$

Cyclohexane : $0.7786 \text{ g/ml} \times \frac{1000 \text{ ml}}{\text{L}} \times 12 \text{ L} = 9343.2 \text{ g}$

Try to wash in one stage? 22L

$$\frac{22,000 \text{ g}}{14,073 \text{ g}} = \frac{0.336 - x_{n1}}{x_{n1} - 0}$$

$$\begin{aligned} 22,000 x_{n1} &= 4729 - 14,073 x_{n1} \\ 36,073 x_{n1} &= 4729 \\ x_{n1} &= 0.13 \end{aligned}$$

Looks like we'll have to do the washing in more than 1 stage since the carboy only holds a total of 50L and the 22L of water only yields an extract that has 18% mass $\text{C}_2\text{H}_4\text{O}_2$ (wpt = 5)

Let's try the extraction in two stages.
 1st stage \rightarrow 10L
 2nd stage \rightarrow 7L

1st stage : $\frac{10,000 \text{ g}}{4,073 \text{ g}} = \frac{0.336 - x_{n1}}{x_{n1} - 0}$

$$\begin{aligned} 10,000 x_{n1} &= 4729 - 14,073 x_{n1} \\ 24,073 x_{n1} &= 4729 \\ x_{n1} &= 0.20 \end{aligned}$$

$$E_1 = \frac{24,073(0.20 - 0.01)}{0.33 - 0.01} = \frac{4574}{0.32} = 14,294 \quad \therefore R_1 (F_2) = 9779 \text{ g}$$

2nd stage : $\frac{7,000 \text{ g}}{9,779 \text{ g}} = \frac{0.01 - x_{n2}}{x_{n2} - 0}$

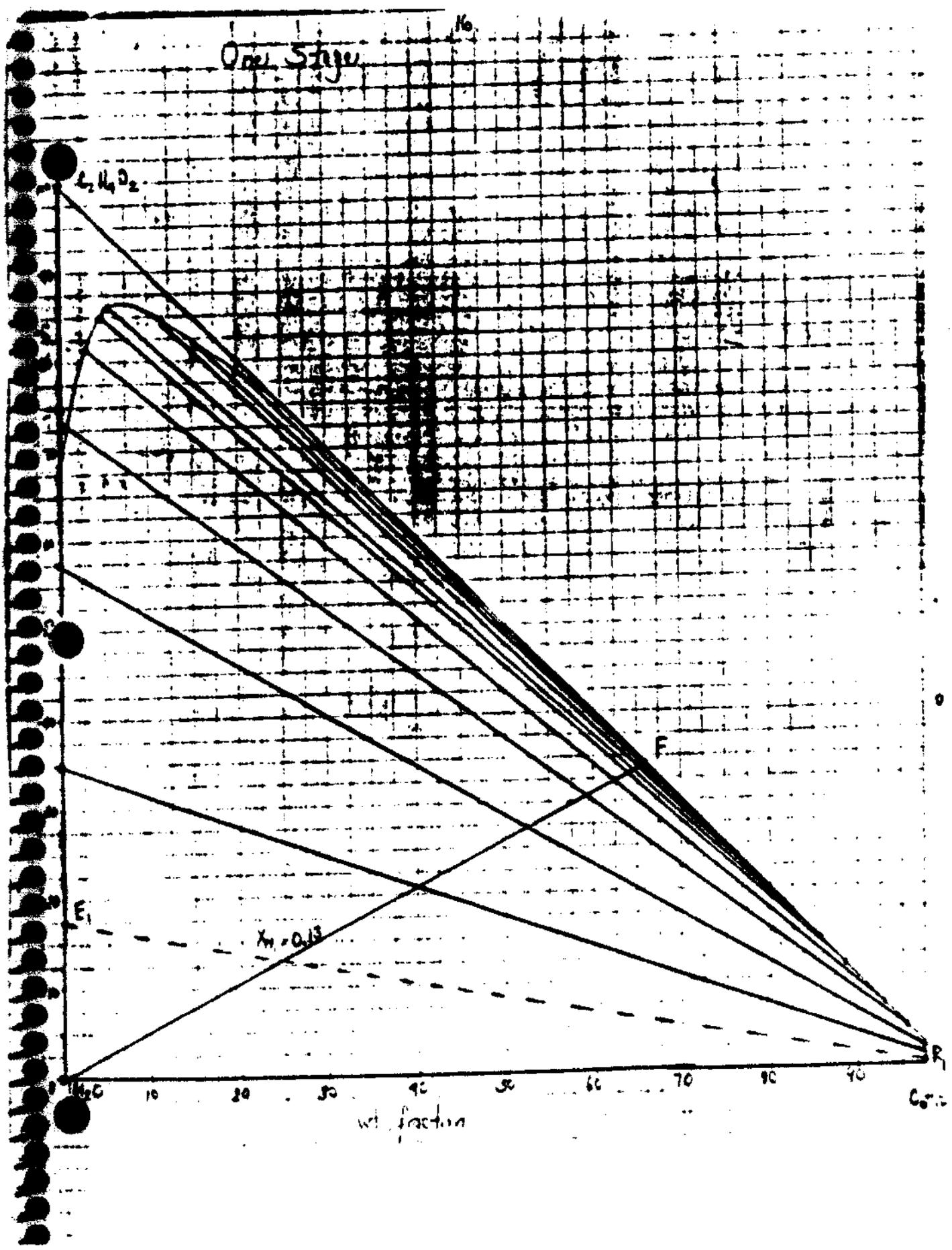
$$\begin{aligned} 7,000 x_{n2} &= 99 - 9779 x_{n2} \\ 16,779 x_{n2} &= 99 \\ x_{n2} &= 0.0058 \end{aligned}$$

$$E_2 = \frac{16,779(0.0058 - 0)}{0.0125 - 0} = \frac{97.52}{0.0125} = 7794 \quad \therefore R_2 = 8994 \text{ g}$$

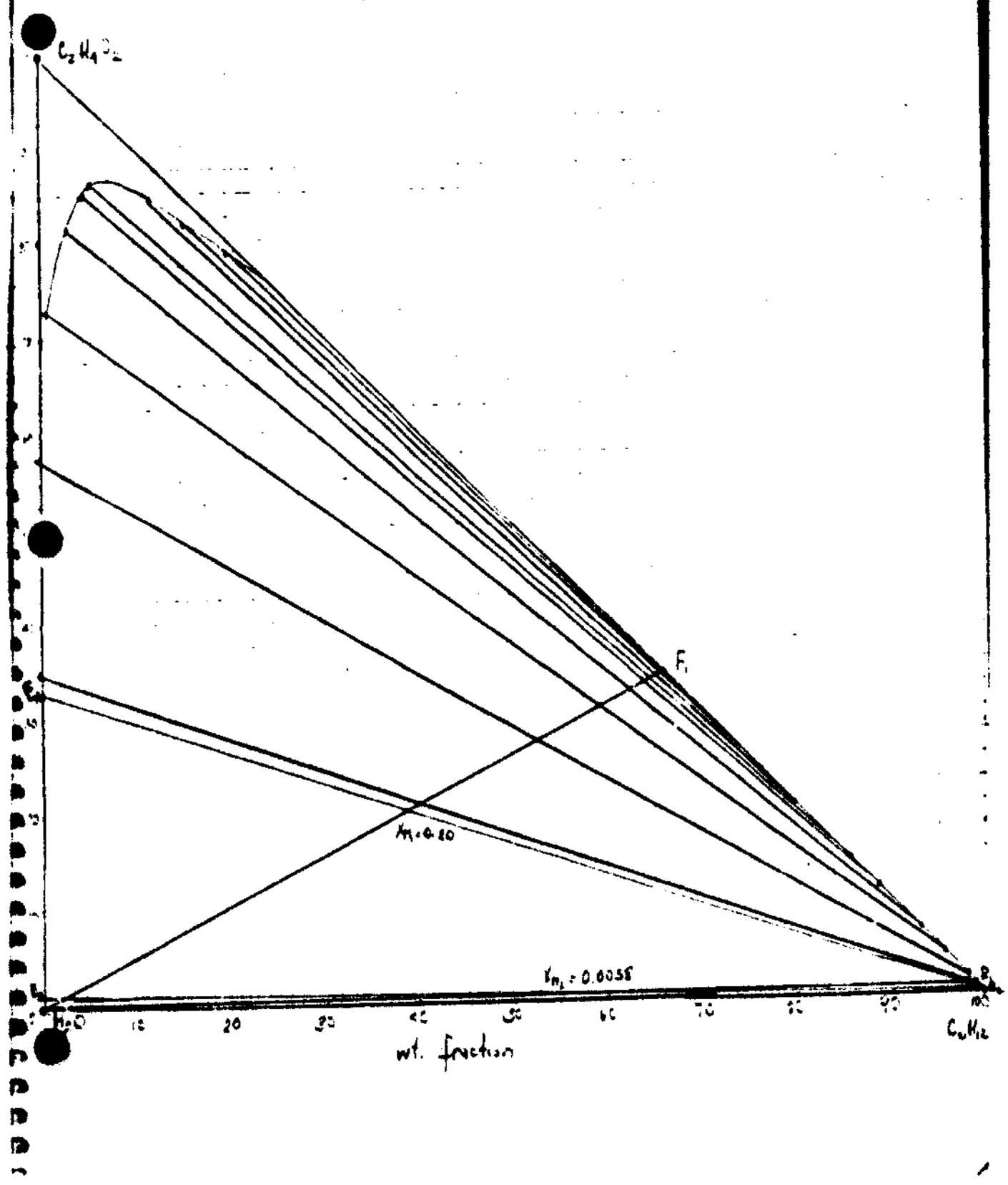
The low indicates that extract will have about 1.25 mass% acetic acid. This corresponds to pH = 4.5.

\Rightarrow Extraction will work in two stages : 10L ... then 7L of water

One Stage



Two Stages



<u>EQUIPMENT NEEDED FOR CHEM.E. 292/390</u>	<u>COST</u>
50L Nalgene carboy	70.50
Teflon paddle, 15.2cm long	101.90
Teflon coated stainless steel shaft, 0.9m long	215.65
Teflon jacket, 8in. (5.35/in.)	42.80
plastic pipe adapters, 5 (0.40/adapter)	2.00
Teflon tubing, 9.5ft. (5.50/ft.)	52.25
Plexiglass cylinder, 6in. OD, 28in. long	90.00
10L Nalgene carboy	43.15
Cyclohexane, 4*1gallon bottles	112.00
Intalox saddles	?
HSi(OMe) ₃ , 1L	422.20
Nalgene Spigot	12.00
Polypropylene Safety Trays, 2	85.00
GRAND TOTAL.....	\$1250.00