

ETHYLENE PRODUCTION
CONTINENTAL OIL COMPANY
CHEMICALS DIVISION ORIENTATION

I. INTRODUCTION

The objective of this discussion is to acquaint all of you with: (1) the growth and use of ethylene since the beginning of commercial production in the early 1930's, (2) the development of ethylene technology and the resulting impact on ethylene plant size and economics, and, (3) specifically, Continental Oil Company's development, design, erection, startup, and future development of its 500 MM Lb/Yr plant which was brought on stream at Lake Charles, Louisiana, in February of 1968.

II. ETHYLENE HISTORY

The first significant world demand for ethylene manufacture began in the United States in the early 1930's. The almost unbelievable growth (17 1/2 percent per year since 1942 worldwide) of the ethylene market has been due to ethylene being a source for several versatile derivatives including: polyethylene, ethylene oxide, ethyl alcohol, styrene, ethyl chloride, and polyvinyl chloride. (See Figure 1 in the appendix.) 1970 North American ethylene production was about 8.7 billion Lbs/Yr (42 percent of the world ethylene capacity) and is expected to reach 21.5 billion Lbs/Yr by 1980 (estimated 33 percent of world capacity). (11) This points out the existing high expansion rate of the ethylene market in Europe and Japan.

Petroleum companies have, since the beginning of the ethylene industry, been in a sound position for supplying feedstock for the manufacture of ethylene. The manufacture of ethylene in the 1930's was based on the separation of ethylene from petroleum refinery offgases (typically 8-16 mole percent ethylene). The growing demand for ethylene production and the reluctance of the refiner to obligate himself to guarantee uniformity of supply and

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an ethane cracking plant (deleting the 90 mole percent propane feedstock flexibility), and the deletion of the C₃ splitter, Lummus was awarded the contract for \$18.066 MM on May 27, 1966.

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composition of feed gas over a long period dictated that cracking technology be developed to utilize light hydrocarbons as feedstock. Since components such as ethane and propane were valued as fuel, the way was open for the economic development of furnace cracking technology.

Conoco Petrochemical management was keenly interested in the ethylene market and Research and Development in Ponca City was working closely with the M. W. Kellogg Company in the early 1960's to develop a process for vinyl chloride monomer (VCM) manufacture as an outlet for ethylene. The Conoco development work which led to the startup of the "ALFOL" alcohol plant at Lake Charles in 1962 provided a base for ethylene consumption of about 60 MM Lbs/Yr which has expanded to the present consumption of about 130 MM Lbs/Yr.

In May of 1962, Mr. A. J. Morse issued a report reviewing the technology and processes for producing ethylene. The possibility of partnership with The Stauffer Company in a VCM joint venture increased the Conoco interest in ethylene. This joint venture materialized, and the 600 MM Lbs/Yr VCM plant at Lake Charles is now wholly owned by Continental Oil Company following a ruling by The Federal Trade Commission.

Ethylene plant economics were issued between January of 1965 and May of 1966, varying from \$15.6 MM for a 400 MM Lb/Yr plant to \$20.07 MM for a 500 MM Lb/Yr plant including propylene-propane splitter. In June of 1965, bids were received for a 500 MM Lb/Yr plant from Stone and Webster for \$10 MM, The Lummus Company for \$13.3 MM, and the M. W. Kellogg Company for \$12.9 MM. Following evaluations to determine actually what the various bids included, a rebid by Lummus, a Conoco decision to build an ethane cracking plant (deleting the 90 mole percent propane feedstock flexibility), and the deletion of the C₃ splitter, Lummus was awarded the contract for \$18.066 MM on May 27, 1966.

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"high severity" cracking furnaces. Lummus had just, in the spring of 1967, put into operation a 750 MM Lb/Yr ethane cracking plant for duPont at Orange, Texas. The combined Conoco-Lummus effort was aimed at a smooth startup. Conoco spent some \$100,000 in extra engineering and inspection costs prior to startup.

Following checkout, alignment of the compressors, complete dryout of the process units with hot natural gas and nitrogen, and dryout of the cold sections with methanol, hydrocarbon feed was started to two of the cracking furnaces on February 2, 1968. Specification ethylene was cut to the product pipeline on February 11. This was one of the smoothest startups of any ethylene unit of this size, and it was well publicized by Lummus in The Oil and Gas Journal, Chemical Engineering, and other publications.

The organization of the Lake Charles ethylene unit is as follows:

Plant Superintendent - Mr. Richard A. Conrad
Operations Superintendent - Mr. Richard A. Darling
Operations Supervisor - Mr. Basil Drymon
Process Engineer - Mr. Gary Foshee

III. RECENT ETHYLENE TECHNOLOGICAL ADVANCEMENTS

The Lummus design of our 500 MM Lb/Yr ethylene unit at Lake Charles was significantly influenced by recent advances in process technology. The more important advances have been in the cracking furnace, charge gas compression, and refrigeration sections of the plant. This technology has had a considerable impact in ethylene economics which will be discussed in Section IV. Perhaps the most important developments have been in the cracking furnace design which has resulted in increased ethylene production capabilities per furnace while increasing furnace run lengths between decokings. Because the cracking furnace section is essentially the heart of ethylene manufacture, some details of the furnace technology will be discussed herein.

The cracking furnace run lengths between decokings have been the greatest disappointment in the operation of the Lake Charles ethylene plant. Lummus had guaranteed a furnace run length between decokings of 90 days. Early

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secondary condensate-forming reactions.⁽²⁾

The "high severity" concept for ethylene production has significantly altered the design of cracking furnaces. Conventional cracking furnaces are designed for heat fluxes of 8000-12,000 BTU/Hr/Sq Ft.⁽³⁾ The furnaces operating at Lake Charles generate average fluxes around 25,000 BTU/Hr/Sq Ft with a residence time in the cracking section of about 0.5 seconds. Figure 3 in the appendix illustrates the layout of tubes and burners in the radiant section of the Conoco ethane cracking furnaces. These higher heat fluxes require improved materials for furnace tube manufacture that will continually operate at temperatures near 1900 °F. Typical tube material is a 25 percent

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plant experience demonstrated run lengths of 20 days and improvements based on operating experience led to a settlement with Lummus that 50-day run lengths were possible although to date this has not been a matter of practice and 35-day run lengths are common.

The formation of coke in the furnace tubes was rationalized for years by the "film" theory. Furnace designers, applying an analogy to heat transfer, theorized that a thin film of hydrocarbons slides along the inside walls of the furnace tubes and that a big part of the temperature drop between the tube wall and the bulk fluid reaction temperature takes place across this film. Therefore, an increase in heat flux, meaning a rise in tube wall temperature, results in a corresponding increase in film temperature. Experts predicted film temperatures high enough to cause the film of hydrocarbons to form coke. One means of coke prevention seemed to be lower tube wall temperatures by using less heat flux and longer residence time for the reactions. The Lummus Company in 1959 while running pilot plant tests to explain results of tests on a commercial cracking furnace discovered that lowering the firing rates and increasing the residence time actually increased rather than decreased coke formation rates as would be expected from the "thin film" theory. A new line of thinking toward coke formation theory results which rationalizes that tube wall coke results from secondary reactions that yield multiple ring condensation products such as naphthalene. These products have high boiling points, tend to collect on tube walls where they are cracked to extinction, or coked, by high temperatures. Shorter residence time (more heat) favors primary olefin-forming reactions, not secondary condensate-forming reactions.⁽²⁾

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chromium-20 percent nickel alloy known as HK-40.

The process effect of the "high severity" cracking has been to increase furnace ethylene capacity from about 30 MM Lb/Hr to 100 MM Lb/Hr when cracking a light hydrocarbon feedstock. The "high severity" cracking is reported by the suppliers to reduce the by-product formation, thus improving ethylene yields. Because naphtha cracking produces the larger by-product ratios, the new cracking furnaces have a more pronounced effect on naphtha crackers than on ethane crackers. (See Figures 4 and 5 in the appendix.) Table I (page 6 in the appendix) summarizes our test run yields at Lake Charles compared to Lummus' predicted yields. Also shown for comparison in Table I is ethylene yield data developed by Dr. H. C. Schutt, Consulting Engineer, Boston, and Dr. C. V. Foster of Continental Oil Company.

In addition to the advances in furnace technology, ethylene plant designers have made substantial reductions in compressor-horsepower requirements. This has been possible because of the richer furnace effluent compositions as well as improved efficiency of the larger compressor units. Compressor requirements for efficient plants have been reduced from about 0.75 Bhp/Lb of ethylene product/Hr to approximately 0.54 Bhp.⁽⁴⁾ This ratio for the Conoco ethylene plant is 0.575.

Reductions in refrigeration compressor horsepower have also been made. The use of an expander in the demethanizer feed chilling system has provided a temperature source lower than that possible with the lowest level of ethylene refrigeration or with Joule-Thomson expansion. This enables the use of the double cascade refrigeration system using propylene and ethylene refrigerants in preference to the triple cascade system using propylene, ethylene, and methane.

IV. PROCESS DESCRIPTION

The following is a brief description of the processing sequence as shown on the overall Process Flow Diagram,

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A. Cracking and Quench

Ethane and propylene-propane recycle are cracked in tubular heaters in the presence of dilution steam to an outlet temperature of 1560 °F. The heater effluents are cooled to 600 °F in transfer line exchangers which generate high pressure steam at 650 psig.

The effluents from the transfer line exchangers are combined and directed to the quench tower. By direct contact water cooling, the greater part of the dilution steam and some heavier hydrocarbons are condensed. Net overhead vapor at 110 °F flows to the compressor system. Quench water plus condensed steam is separated from the condensed hydrocarbons in a quench water surge drum which is operated at 180 °F. The circulating hot water is used to preheat the ethane furnace feed and further cooled in the air cooled quench water coolers and against cooling water. Condensed dilution steam is sent to the process water stripper, where it is stripped of dissolved gases and light hydrocarbons, vaporized against 200 psig steam and reused as heater dilution steam.

B. Charge Compression and Acid Gas Removal

The quench tower overhead vapors are compressed in four centrifugal compressor stages to a pressure of 535 psig, with interstage cooling to 110 °F. Between the third and fourth stages, the gas is treated for acid gas removal in the caustic and water wash tower. The fourth stage discharge is cooled with water and with propylene refrigerant to 60 °F. Liquid condensate is separated and the vapor is sent to the desiccant dryers.

Interstage hydrocarbon and water condensates

from the first three stages are sent back to the quench water surge drum. Fourth stage condensate is recycled to the third stage discharge drum.

1. Drying and Feed Chilling

The final compressor discharge gas at 60 °F and 525 psig is dried in packed bed dryers using activated alumina before passing to the low temperature recovery section. Three dryers are provided. Two are on stream in series, while the third is regenerated. Both regeneration and cooling of the dryers are accomplished using hydrogen rich offgas on a once-through basis. A regeneration heater and a cooler are provided for the regeneration operation.

The dried gas at 60 °F is progressively chilled and partially condensed, with condensate removal at -30 °F, -95 °F, -145 °F, and -185 °F. The remaining vapor is the hydrogen rich offgas. The condensates are fed to the demethanizer. The chilling is achieved with propylene and ethylene refrigeration, vaporizing feed and recycle ethane, and reheating hydrogen and methane offgas streams. An expander is used on the hydrogen rich offgas to provide the lowest level refrigeration. The hydrogen rich offgas and the methane rich offgas are sent to fuel after reheating in the chilling train and against liquid propylene refrigerant.

2. Demethanization and Deethanization

The demethanizer, which operates at 445 psig, has a bottoms temperature of 31 °F and an overhead temperature of -113 °F. The column is reboiled with propylene refrigerant and

reflux is condensed with ethylene refrigerant. The demethanizer overhead is the methane offgas, which is sent to fuel after reheating in the chilling train and against liquid propylene refrigerant. The demethanizer bottoms flow to the deethanizer where C_2 's are separated from the C_3 and heavier fraction. The deethanizer operates at 395 psig with 16 °F and 182 °F overhead and bottoms temperature, respectively. The reboiler utilizes low pressure steam and reflux is condensed with propylene refrigeration. The bottoms product is sent to the depropanizer and the net overhead flows to the acetylene removal system.

3. Acetylene Removal and Ethylene Fractionation

The deethanizer overhead vapor, after feed-effluent exchange and preheat, is sent to the acetylene converter. Acetylene is hydrogenated over a palladium catalyst in a packed-bed reactor. Hydrogen offgas after enrichment, methanation and drying over molecular sieves, is injected into the converter feed to provide the hydrogen requirements. Two vessels are provided, one is on stream while the other is on standby. A fired heater is provided for regeneration. The converter effluent is used to preheat the feed and sent to the ethylene fractionator.

The feed to the ethylene fractionator consists of ethylene, ethane and unreacted hydrogen and methane from the acetylene removal system. The tower operates at 285 psig with overhead and bottoms temperatures of -20 °F and 21 °F, respectively. Condensing and reboiling are done by propylene refrigeration. The ethylene product is withdrawn as a side stream from the tower, and unreacted hydrogen and methane from the acetylene removal system are recycled from the reflux drum to the charge compressor. The liquid ethylene

product is vaporized and delivered to the battery limits at 600 psig and 225 psig.

The fresh ethane feed is dried over molecular sieves, combined with the bottoms ethane product from the ethylene fractionator and vaporized against demethanizer feed. The total ethane vapor stream is superheated against propylene refrigerant and circulating quench water and then charged to the cracking heaters.

4. Fractionation of Propane and Heavier Components

The depropanizer, operating at 160 psig, with 77 °F and 228 °F overhead and bottoms temperatures, respectively, receives feed from the deethanizer bottoms. Steam and propylene are the reboiling and condensing mediums, respectively. The overhead vapor product is recycled to the cracking furnace.* The bottoms product containing C₄ and heavier is sent to the debutanizer.

The debutanizer operates at 65 psig with 119 °F top and 249 °F bottom temperatures. Cooling water is the reflux condensing medium, while steam is used for reboiling. The overhead liquid is the mixed C₄'s product which is sent to battery limits, and the bottoms is the light aromatic distillate product which is cooled to 120 °F and sent to battery limits.

5. Propylene Refrigeration

The propylene refrigeration system is a closed, multi-stage system using a centrifugal compressor. It provides refrigeration at four levels: -35 °F, -5 °F, 37 °F, and 60 °F. The compressor effluent is cooled and condensed against cooling water and subcooled against various produce and process streams. Interstage condensing at the various levels is obtained from reboiling the demethanizer and the ethylene fractionator, and also from the vaporization of the liquid ethane feed and ethylene product.

* The C₃ overhead is now being sold as product and is not recycled to the furnaces.

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6. Ethylene Refrigeration

The ethylene refrigeration system is a closed, multi-stage system using a centrifugal compressor. The ethylene system has three levels of refrigeration: -150 °F, -100 °F, and -65 °F. The compressor effluent is desuperheated against propylene refrigerant and then condensed against the lowest level propylene refrigerant.

The following are the typical values for product unit cost, production rates, and distribution for the Conoco ethylene plant during 1973:

<u>Product</u>	<u>Unit Cost ¢/Lb</u>	<u>MM Lb/Yr</u>	<u>Distribution</u>
Ethane	1.11	819.0	Gillis, Texaco, Union Texas
Tail Gas	0.73	4.8	Lake Charles Refinery
Ethylene	3.50	605.0	VCM, ALFOL, PPG, Others
Butadiene	3.87	27.2	Sold to Mobil Oil Co.
Aromatic Distillate	1.44	23.9	Lake Charles Refinery
Fuel Gas	1.02	133.1	Burned as fuel in plant
Propylene- Propane	1.96	14.5	Sold to Cities Service Oil Co.
Hydrogen	1.93	13.2	ALFOL, NP, Solvent plants

D. Conoco Ethylene Plant Changes

Since initial startup, the ethylene plant capacity has been increased from 500 to 650 MM pounds per year. The most important of these changes involved adding a sixth cracking furnace. Modifications to the turbines on the charge gas and propylene refrigeration compressors greatly increased the capacities of these two machines. Rotating elements and diaphragms were also changed on the propylene compressor.

Other changes include changing trays in the quench tower and demethanizer and changing demisters in several knockout drums. To increase summer capacity

two new cells will be added to the cooling tower.

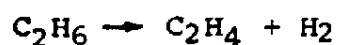
A major operating change which led to a capacity increase was the increased firing which led to a change from 60 to 64 percent furnace conversion (ethane disappearance).

A new compressor was added to send hydrogen to the ALFOL, normal paraffin and solvent units. A propadiene converter was added to purify the propylene-propane stream before sending it to Cities Service.

A coke fine removal system was installed to eliminate water pollution during decoking operations.

V. CHEMISTRY AND REACTION KINETICS

On the surface, the chemistry describing the cracking of hydrocarbons to ethylene seems straight forward and little description beyond the simple cracking reactions seems necessary. For example, the cracking of ethane is simply illustrated by the following reaction:



If this were the case, the reaction products would consist only of ethylene and hydrogen in equimolar quantities. Early experimental work with cracking ethane showed effluent components of hydrogen, methane, ethylene, ethane, acetylene, propylene, propane, C_4 's, C_5 's, and aromatics. To explain these experimental results, F. O. Rice⁽¹⁰⁾ postulated the production of free radicals and he was able to rationalize the distribution of the principal products resulting from cracking of several of the C_2 to C_6 paraffin hydrocarbons at low conversions.

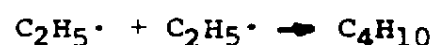
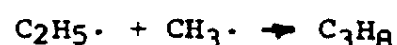
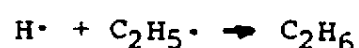
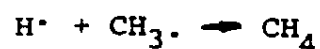
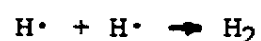
Free radical mechanisms have been a powerful tool in guiding predictions and in formulating correlations for cracking data, but even for the simple ethane cracking reactions it has not yet been possible to rationalize the complete product distribution.

The following equations illustrate the proposed free radical mechanism for ethane cracking:⁽¹⁰⁾

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- (1) $C_2H_6 \rightarrow CH_3\cdot + CH_3\cdot$
- (2) $CH_3\cdot + C_2H_6 \rightarrow CH_4 + C_2H_5\cdot$
- (3) $C_2H_5\cdot \rightarrow C_2H_4 + H\cdot$
- (4) $H\cdot + C_2H_6 \rightarrow H_2 + C_2H_5\cdot$
- (3) $C_2H_5\cdot \rightarrow C_2H_4 + H\cdot$ (Etc)

Reaction (1) is referred to as the initiating reaction, reaction (2) is a transition reaction, and (3) and (4) are chain reactions. If reactions (3) and (4) continued without interruption it would be necessary for only one molecule of ethane to decompose by reaction (1), and all other ethane disappearance would be attributable to reaction (4). However, the chain cycle can be terminated in several ways:



and it is necessary to generate new radicals by reaction (1), (2), and (3) to start a new chain. Everytime a new chain is thus initiated, a molecule of methane is produced by reaction (2) and a molecule of ethylene by reaction (3).

Therefore, of the total moles of ethylene in the effluent, a quantity equal to the number of moles of methane was formed as the result of the chain-initiating reactions, while the remainder can be attributed to the chains. The average chain length can then be estimated by: (10)

$$\text{Average Chain Length} = \frac{\text{Moles } C_2H_4 - \text{Moles } CH_4}{\text{Moles } CH_4}$$

Vapor-phase cracking reactions have been found to be generally independent of both the pressure and the surface to volume ratio in the reactor. Thus the reactions are

considered to follow a first order mechanism: (10)

$$K_t \theta = \ln \left(\frac{1}{1-\alpha} \right)$$

Where $K_t \theta$ = Reaction velocity constant, sec⁻¹

θ = Time, sec

α = Fractional disappearance of reactant

Reaction velocity constants for various light hydrocarbons are shown in Figure 8, page 9, of the appendix. In the cracking furnace it is not possible to instantaneously bring the reactants to the desired reaction temperature. The reactant temperature rises continuously from inlet to outlet of the coil.

Since the temperature and thus the reaction rate is continuously changing, it becomes necessary to consider the time-temperature history of the reactants in order to calculate $\int K d\theta$ for the entire coil and thereby to predict the conversion at the outlet.

The term "equivalent time" can be used for prediction of outlet component temperature or conversion conditions for a particular feedstock. The "equivalent time" is the time which, if the reactant could be raised instantaneously to the reference temperature and held there, would produce the same degree of disappearance as achieved in the actual variable-temperature furnace.

$$(\theta_{eq})_t = \frac{\int K d\theta}{K_t}$$

Where $(\theta_{eq})_t$ - Equivalent time, sec, at temperature t
 K_t = Reaction velocity constant at temperature

Using Figure 9, page 10, in the appendix, suppose a cracking furnace is designed to convert 60 percent of ethane at a coil outlet temperature of 1520 °F. From Figure 9 at 60 percent conversion, $K = 0.92$ and K for ethane at 1520 °F = 2.0 (Figure 8, page 9). Thus:

$$(\theta_{eq})_t = \frac{0.92}{2.0} = 0.46 \text{ secs}$$

VI. ETHYLENE ECONOMICS AND CONOCO'S FUTURE PLANS

Ethylene has historically been produced in the United States from ethane and propane. Heavy liquid (naptha) feedstock is expected to increase from 20 percent today to half of the ethylene production in 1980.

The large quantity of by-products and ratio of feedstock to product for a naptha-based plant makes the price much larger than that of an ethane-based plant. Conoco estimates that the investment per pound of ethylene is 60 percent greater for a naptha-based plant than for an ethane-based plant.

With nearly 60 percent of its income derived from ethylene, VCM, and PVC, Conoco Chemicals is considering increasing its ethylene production. At this time the smallest investment is for expansion of the existing ethylene plant. These expansion plans are presently being held up because of a lack of ethane. If ethane becomes available this expansion will be considered again.

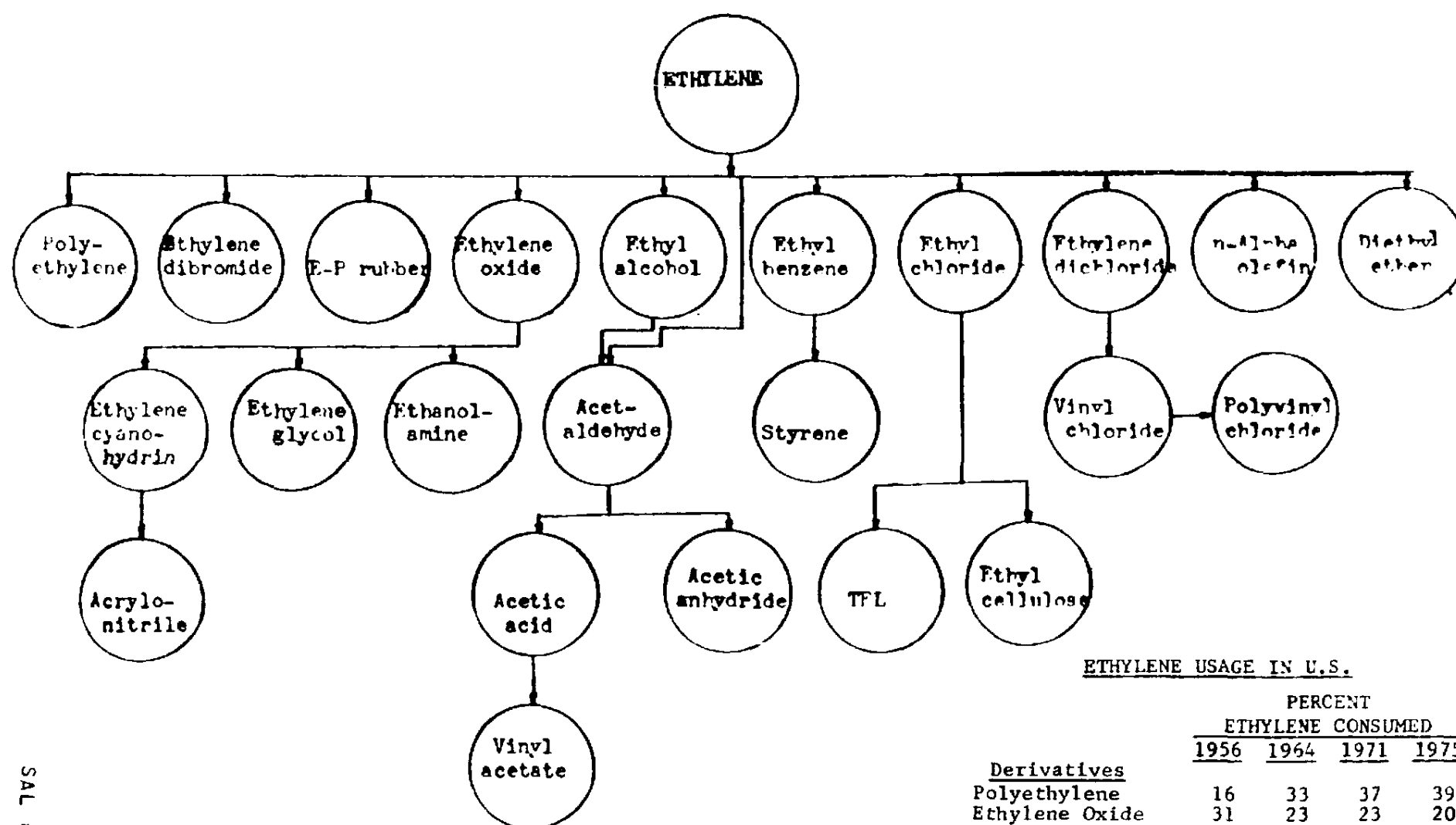
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- (4) "A Decade of Progress in the Manufacture of Ethylene," THE OIL AND GAS JOURNAL, (November 28, 1966), page 65.
- (5) "Preliminary Economics - Ethylene Plant - Lake Charles, Louisiana," PROCESS ENGINEERING DEPARTMENT, November 8, 1965.
- (6) "Ethylene Capacity to Rocket in 1970's," THE OIL AND GAS JOURNAL, November 11, 1968, page 53.
- (7) "Expansion Programs are Geared to 77 Annual Additional Capacity," THE OIL AND GAS JOURNAL, December 5, 1966, pages 109 and 110.
- (8) "Ethylene," CHEMICAL WEEK, November 13, 1965, page 78.
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- (10) "How Cracking Proceeds in the Ethylene-Pyrolysis Reaction," THE OIL AND GAS JOURNAL, June 26, 1967, page 96.
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APPENDIX

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ETHYLENE USAGE IN U.S.

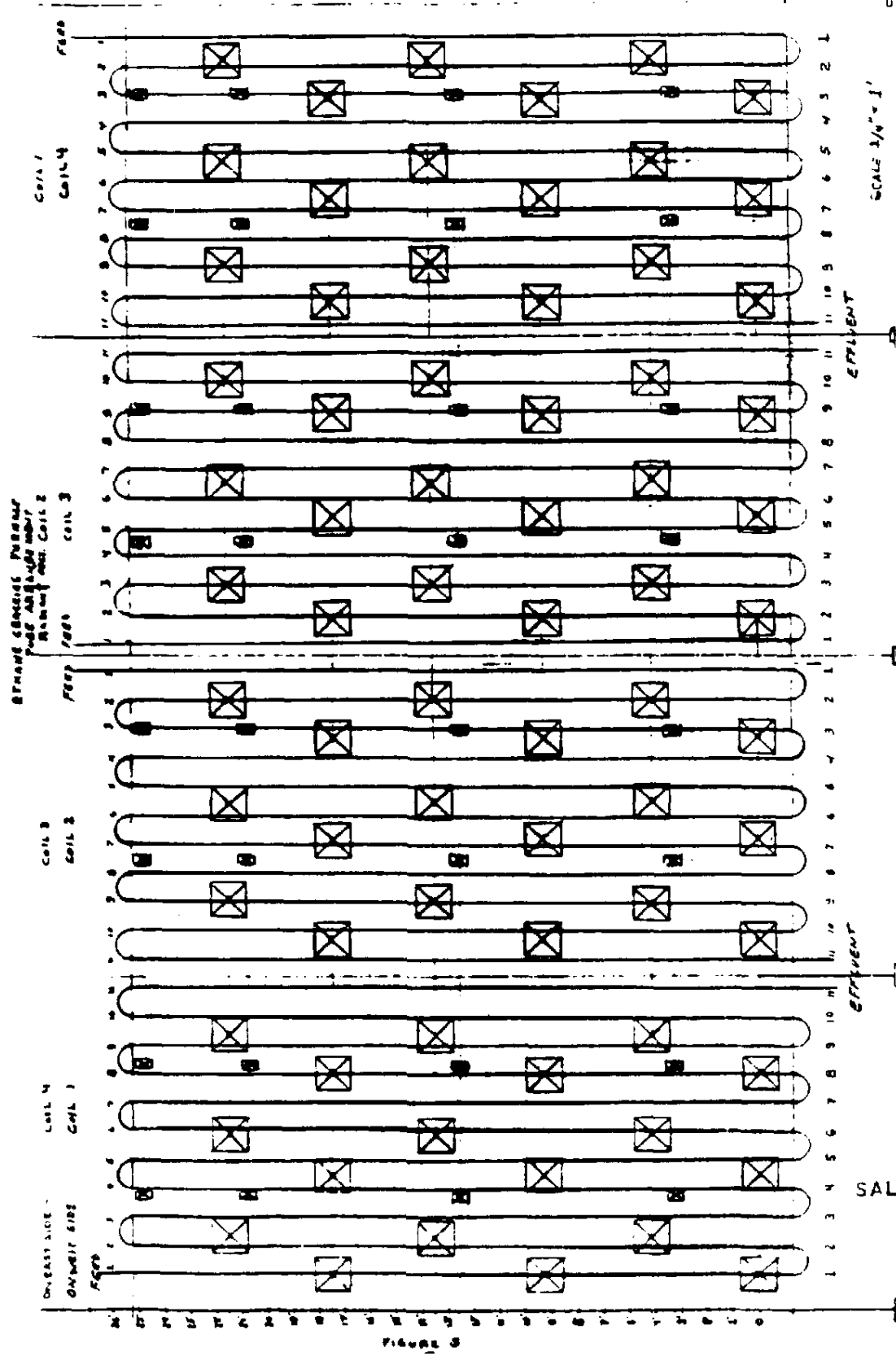
Derivatives	PERCENT ETHYLENE CONSUMED			
	1956	1964	1971	1975*
Polyethylene	16	33	37	39
Ethylene Oxide	31	23	23	20
Ethyl Alcohol	23	15	8	6
Styrene	11	9	9	9
PVC	-	-	12	12
Others	19	20	11	14
	100	100	100	100

*Estimated

FIGURE 1⁷
DERIVATIVES COMMERCIALY PRODUCED FROM ETHYLENE

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ST. DATE SUBJECT SHEET NO. OF
 CHD. BY DATE JOB NO.



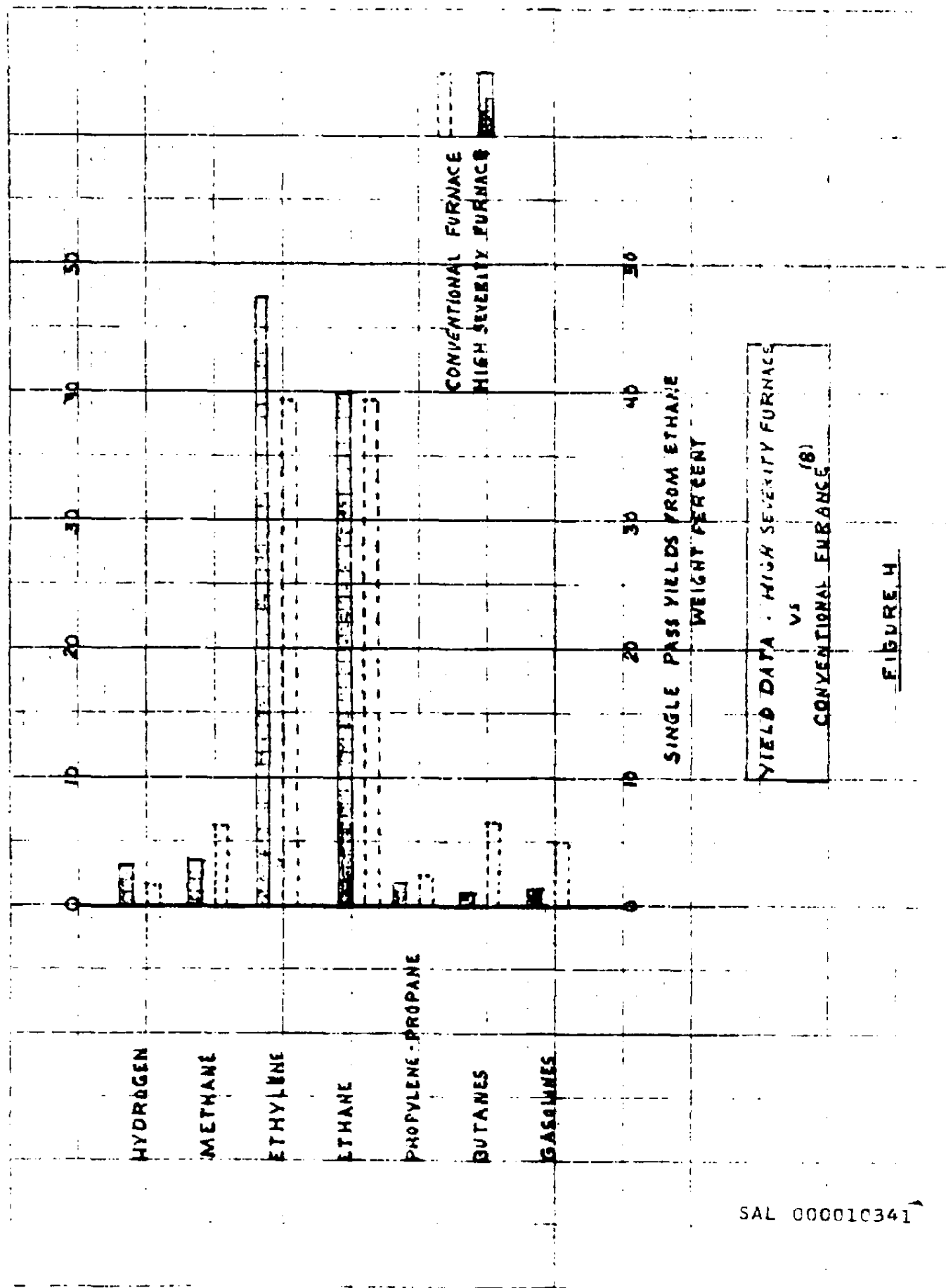
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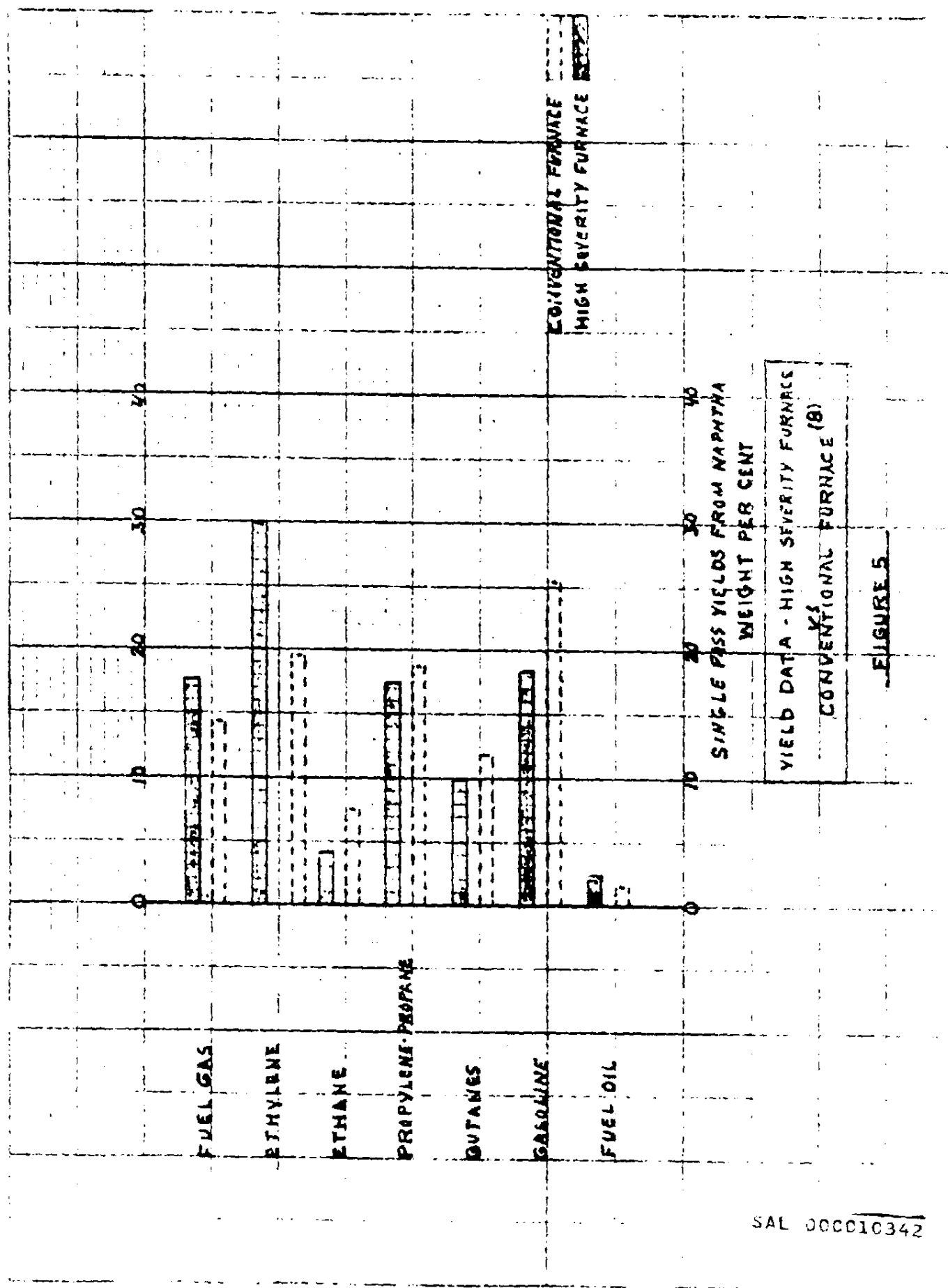
SCALE 3/4" = 1'

FIGURE 3
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TABLE I
COMPARISON OF ETHYLENE YIELDS FROM ETHANE CRACKING
58 PER CENT ETHANE CONVERSION

	<u>Lummus Company</u> <u>July 14, 1967</u>	<u>Foster Schutt</u> <u>Data</u>	<u>July Test</u> <u>Run Data</u>
H ₂	0.0351	0.0344	0.0342
C ₁	0.0391	0.0432	0.0468
C ₂ ⁼	0.0035	-	0.0024
C ₂ ⁻	0.4652	0.4590	0.4521
C ₂	0.4200	0.4200	0.4200
C ₃ ⁼	0.0005	-	0.0005
C ₃ ⁻	0.0122	0.0080	0.0079
C ₃	0.0025	0.0043	0.0003
C ₄ ⁼	0.0072	0.0181	0.0133
C ₄ ⁻	0.0016	0.0181	0.0036
C ₄	0.0022	0.0181	0.0022
C ₅ ⁺	<u>0.0109</u>	<u>0.0130</u>	<u>0.0167</u>
	1.0000	1.0000	1.0000

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11-14-73 TITLE ETHYLENE YIELDS

CONTINENTAL OIL COMPANY
CALCULATION SHEET

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	SINGLE PASS YIELDS		ULTIMATE YIELDS		
	ETHANE	PROPANE	ETHANE RECYCLE	ETHANE + C ₃ RECYCLE	PROPANE + C ₃ RECYCLE
HYDROGEN	3.640	1.466	6.067	6.106	2.133
METHANE	4.017	24.011	6.695	7.484	29.570
ACETYLENE	0.450	0.468	0.750	0.762	0.419
ETHYLENE	47.649	34.227	79.415	80.335	45.392
ETHANE	40.000	4.992	—	—	—
PROPADIENE	0.067	0.463	0.112	—	—
PROPYLENE	1.427	11.908	2.378	—	—
PROPANE	0.283	10.000	0.488	—	—
i-BUTANE	—	0.053	—	—	0.053
BUTADIENE	0.755	3.496	1.258	0.136	4.354
BUTYLENE	0.168	1.463	0.280	0.317	1.760
n-BUTANE	0.174	0.053	0.290	0.290	0.066
PENTANE +	1.360	7.400	2.267	4.570	16.253

YIELDS IN POUNDS PRODUCT PER 100 POUNDS FEED

DATA FROM LUMMUS COMPANY

ACCEPTABLE FOR FEEDSTOCK COMPOSITION RANGES:

ETHANE 85-100 MOL %
PROPANE C-10 MOL %
METHANE C-15 MOL %

REACTION CONDITIONS 1560°F ~ 30 PSI

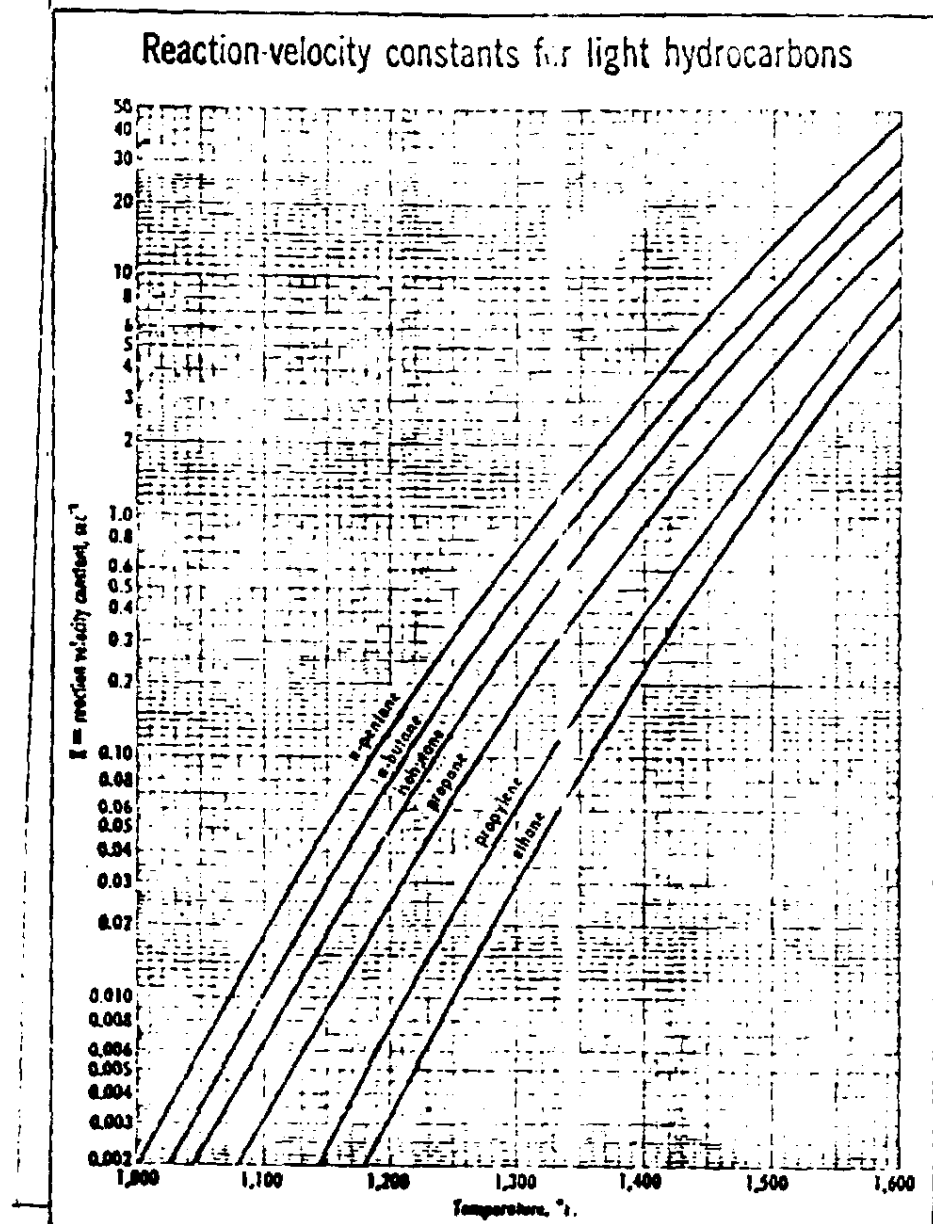


Figure 3(10)

SAL 000010345

Graphical solution of first-order reaction equation

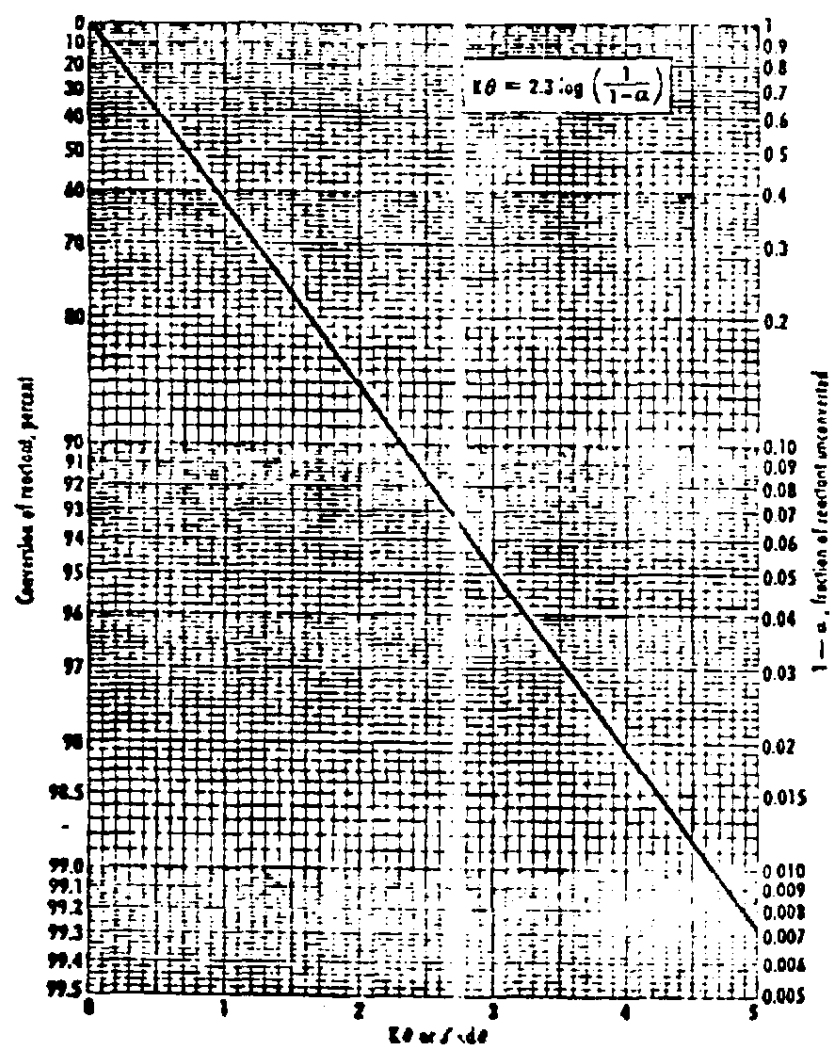
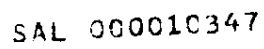


Figure 9 (10)

MANAGER,
LAKE CHARLES OPERATIONS
CONOCO CHEMICALS
L. B. JOHNSON

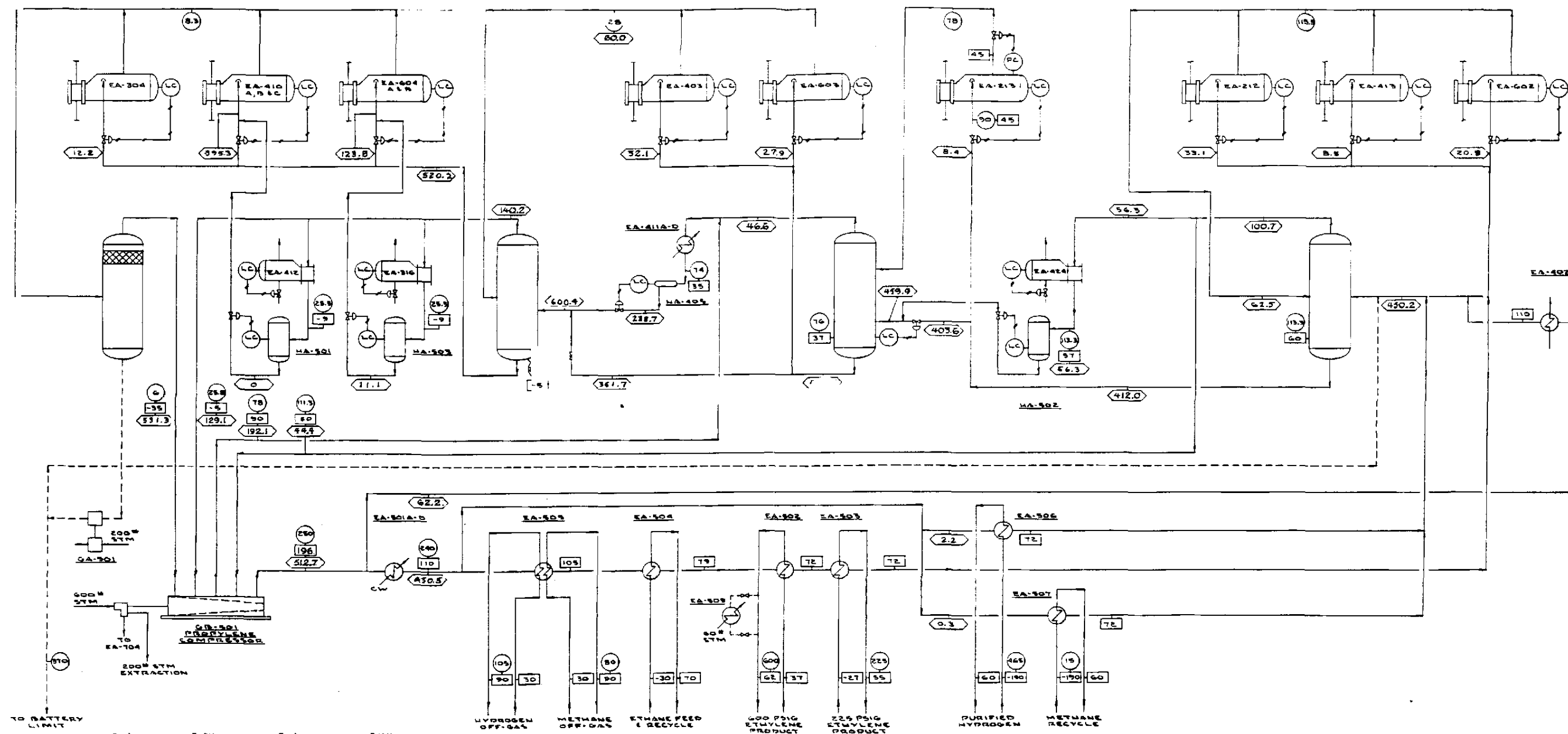


EA-301
PROPYLENE
REFRIGERANT
1ST STAGE DRUM

EA-302
PROPYLENE
REFRIGERANT
2ND STAGE DRUM

EA-303
PROPYLENE
REFRIGERANT
3RD STAGE DRUM

EA-304
PROPYLENE
REFRIGERANT
4TH STAGE DRUM

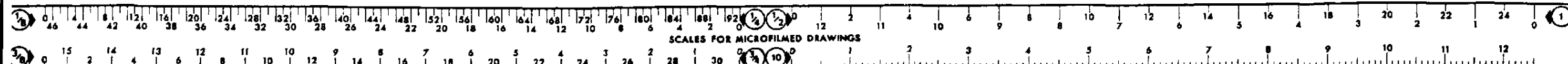


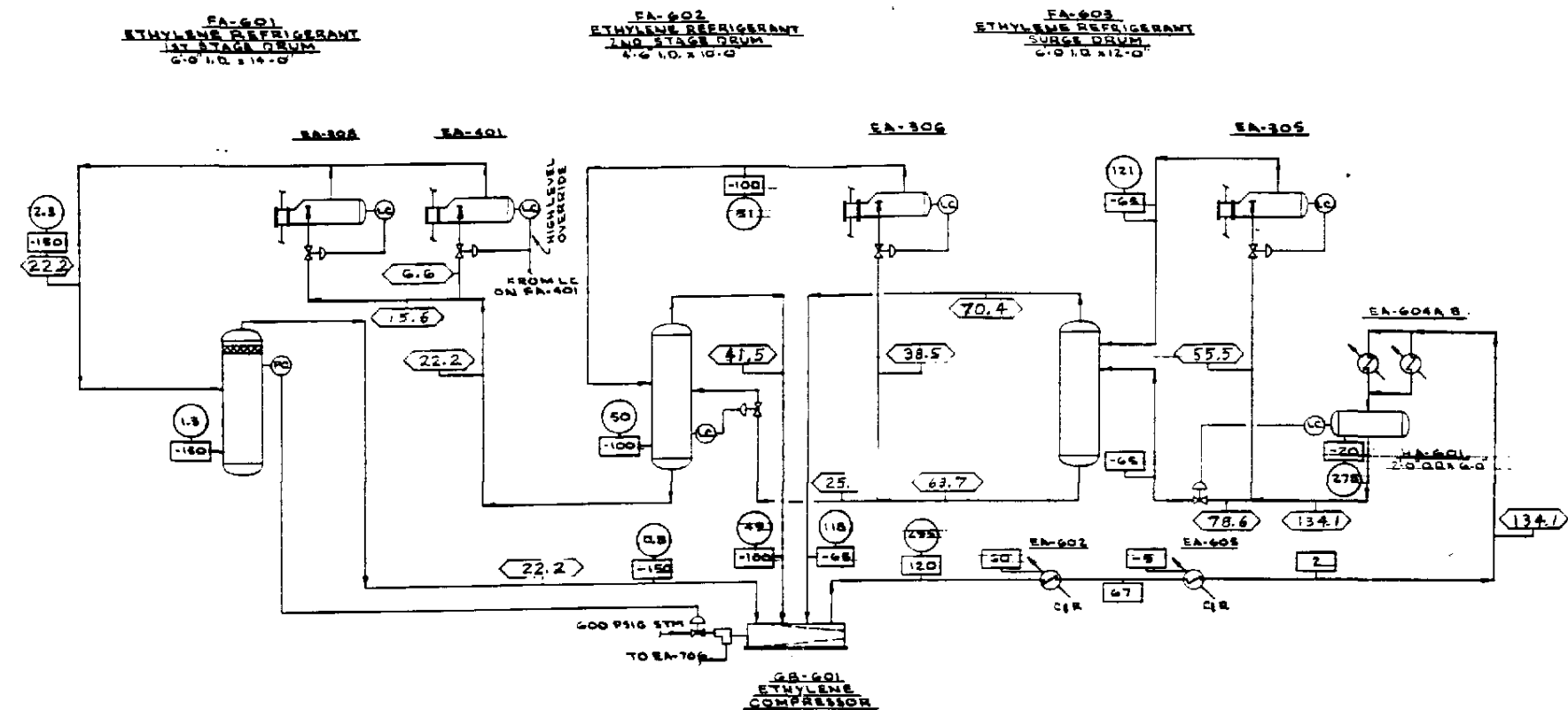
Exchanger No.	Duty, M.B.T.U./Hr.	Exchanger No.	Duty, M.B.T.U./Hr.
EA-212	4,622	EA-424	8,603
EA-213	1,220	EA-501	74,410
EA-304	1,983	EA-502	2,000
EA-316	1,874	EA-503	(1,360)
EA-402	11,075	EA-504	8,508
EA-403	4,710	EA-505	1,544
		EA-506	54
EA-410	64,150	EA-507	7
EA-411	44,220	EA-602	2,921
EA-412	(5,041)	EA-603	4,083
EA-413	1,187	EA-604	20,087

LEGEND

○ PRESS., PSIG
 □ TEMP., °F
 ◇ FLOW, MCM/HR

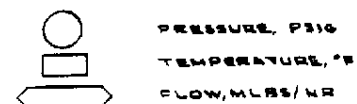
ISU DATE	DESCRIPTION	EXTD PER	MC
		BY CKD	APD
CONTINENTAL OIL COMPANY ENGINEERING CENTER PONCA CITY, OKLAHOMA			
PROCESS FLOW DIAGRAM PROPYLENE REFRIGERATION SECTION ETHYLENE PLANT EXPANSION LAW, CHARLES, L.A. USE BORDER SCALE:			
APPD:	No. 501412-42-5-D		
DATE:			



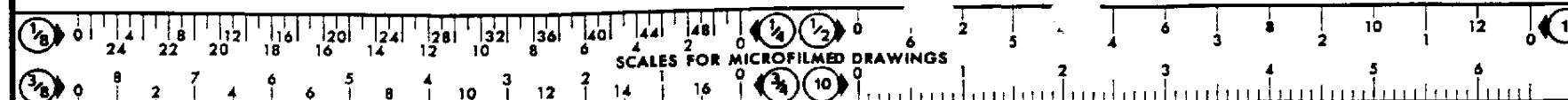


Exchanger No.	Duty, M.B.T.U./Hr.
EA-306	5,989
EA-305	7,301
EA-308	2,596
EA-401	1,044
EA-602	2,921
EA-603	4,069
EA-604A and B:	20,667

LEGEND



ISU	DATE	DESCRIPTION	BY	CKD	APD
CONTINENTAL OIL COMPANY ENGINEERING CENTER PONCA CITY, OKLAHOMA					
PROCESS FLOW DIAGRAM ETHYLENE REFRIGERATION SECTION ETHYLENE PLANT EXPANSION LAKE CHARLES, LA.					
USE BORDER SCALE:					
APPD:		No. SD1412-42-2-C			
DATE:					



PROCESS ENGINEERING TRAINING PROGRAM
CONOCO CHEMICALS

HAMMOND SULFONATION PLANT
MANAGER - JOHN B MAHER
PRODUCTION RATE - 30 MM LB/YR ACTIVE

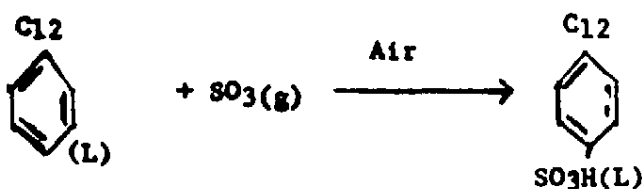
RAW MATERIALS - "MALKYLENE" 500 alkyl benzene
"ALFONIC" 1618c alcohol
Sulfur Trioxide, Sodium Hydroxide, Ammonium Hydroxide,
and water.

PRODUCTS - Detergent Intermediates
Alkyl benzene sulfonic acid
Alkyl benzene sodium sulfonate
Ethoxylate sodium sulfate
Ethoxylate ammonium sulfate
Alcohol sodium sulfate

DEFINITIONS - Wt.% Active: wt.% sulfonate or sulfate in final product
Wt.% Oil: wt.% unreacted organic in final product
RCD: Relative color density of 4% active solution

CHEMISTRY - I. Sulfonation - Sulfation, $\Delta H_f = \frac{-72,000 \text{ BTU}}{\text{LB.-Mole SO}_3}$ (very fast, exthothermic reaction)

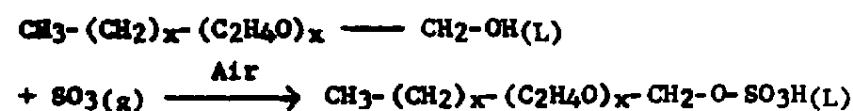
a. Alkyl benzene sulfonation



b. Alcohol sulfation

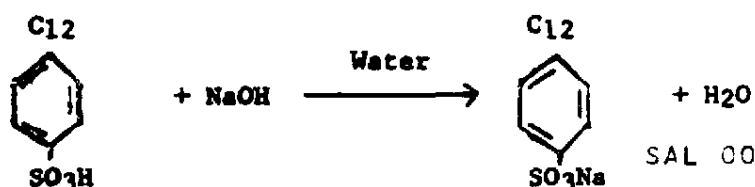


c. Ethoxylated alcohol sulfation



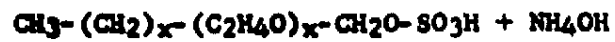
II. Neutralization $\Delta H_f = \frac{-24,100 \text{ BTU}}{\text{LB.-Mole H}_2\text{O}}$ (exthothermic)

a. Alkyl benzene sulfonate



SAL 00001C351

b. Ethoxylate sulfate



CHEMICAL ENGINEERING

I. Sulfonation - sulfation reactor

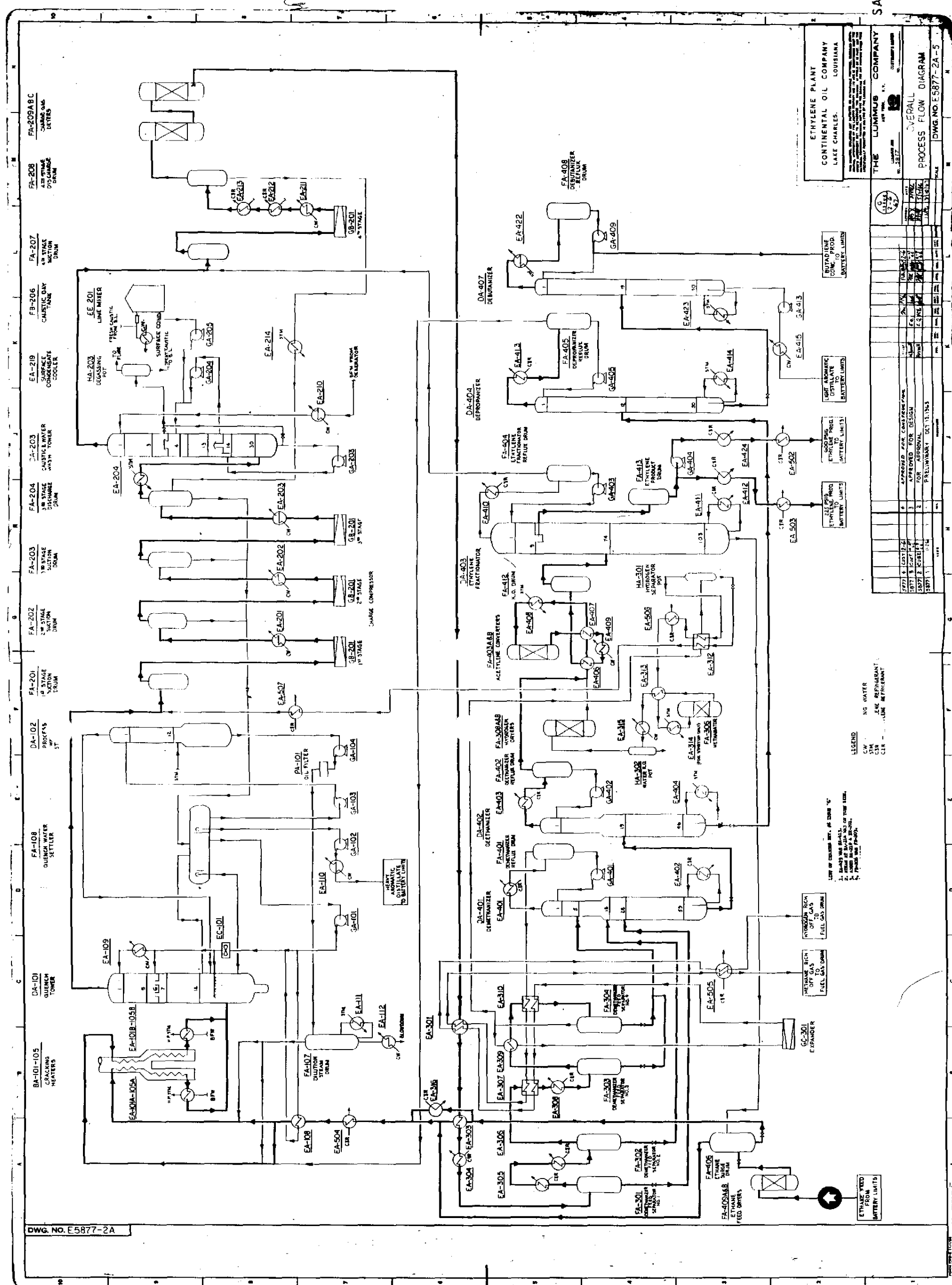
Continuous CO-Current annular flow.
Organic distributed on thin film on inside of metal tube with SO_3 -air gas core mixture propelling the organic in co-current flow. Liquid film velocity, 1-5 ft/sec. Gas velocity, 200 ft/sec. SO_3 gas reacts with organic liquid film producing high heat and mass transfer rates. Air is carrier gas and does not react. Heat is removed through metal wall into cooling water jacket.

II. Neutralization Reactor

Tubular reactor with high recycle rate. Neutralization mixing and reaction take place in head of centrifugal pump. Unit pH control. Non-newtonian fluid flow, high viscosities. Final product is aqueous mixture of sulfonate or sulfate.

(GRJ/1/2/69)

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SAL 00001035

ETHYLENE PLANT
CONTINENTAL OIL COMPANY
LAKE CHARLES. LOUISIANA

THE LUMMUS COMPANY

OVERALL

PROCESS FLOW DIAGRAM

2

2021
11/20/2019

ATE 2021

ATE 2021

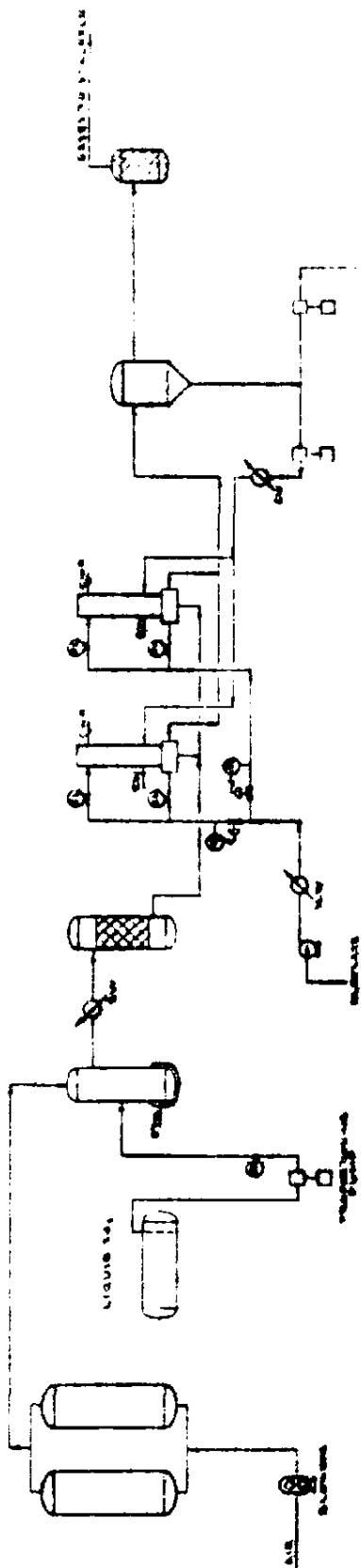
ATE 2021

ATE 2021

ATE 2021

ATE 2021

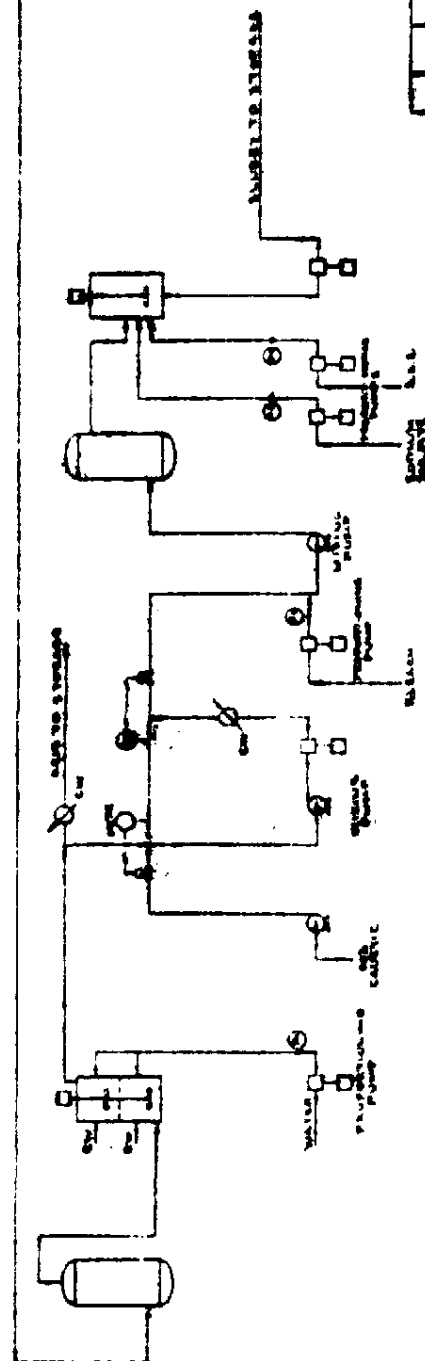
ATE 2021



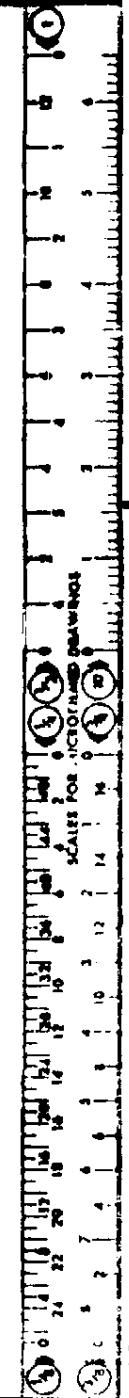
REMARKS

REMARKS

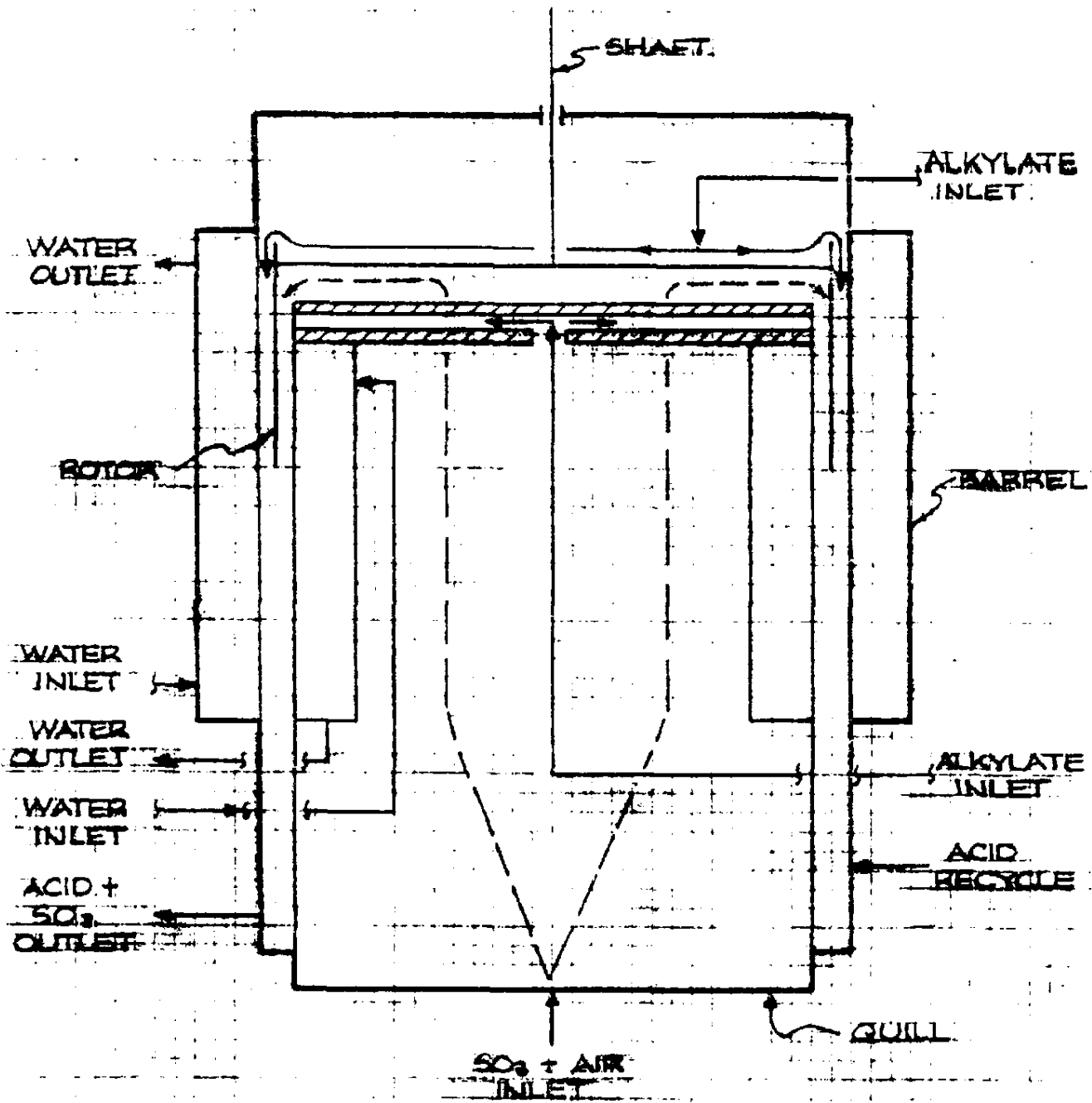
REMARKS



NO.	DATE	DESCRIPTION	BY	CHKD	APPD
1	11/20/2019	CONTINENTAL OIL COMPANY ENGINEERING CENTER POMBA CRT, BEJING			
APPROVED: [Signature] DATE: 11/20/2019					



SAL 000010353



HAMMOND
SULFONATION
REACTOR

PED TRAINING		Z	QWC	I	11-13-73
4-280 S	APPROVED	DMJ	CKD	RSJ	DATE
CONTINENTAL OIL COMPANY		No. SD 1525-42- -A			

SAL 000010354