TRAINING PROGRAM

SECTION 550 - ALUMINA

"ALFOL" ALCOHOL UNIT

LAKE CHARLES, LOUISIANA

INTRODUCTION

Conoco recently decided to start producing CATAPAL-SB alumina at our Lake Charles Chemical Plant. CATAPAL-SB is the trade name for the high purity, high surface area, powdered alumina which is currently being produced by Condea, a German company which is 50 percent owned by Conoco. This alumina is produced as a by-product of Conoco's primary alcohol ("ALFOL") process. In order to produce this alumina in the Lake Charles "ALFOL" Unit, the existing Section 500 which reacts alkoxide with sulphuric acid producing alum and alcohols will have to be replaced by a new Section 550. Section 550 will react the alkoxide with water forming alumina and alcohols. Start-up of section 550 is slated for November 1, 1976.

Since this alumina is produced as a by-product, a basis of 240 MM lb/yr of alcohol resulting in approximately 40 million pounds of CATAPAL-SB per year was selected. The plant's production should exceed 220 million pounds of "ALFOL" alcohols this year.

The value of CATAPAL-SB alumina lies in its very high purity and its special physical properties (see Table I). Because of processing steps intrinsic to Conoco's primary alcohol process, much lower iron, sodium, and silicon concentration specifications can be met than by conventional methods for producing alumina. The low sodium and iron concentrations are particularly important for some catalyst applications.

The unique physical properties of CATAPAL-SB are a result of the one particular difference between Conoco's process and other conventional processes for alumina catalyst-support production. This difference is that the alumina is produced as a fairly dilute wet slurry which is spray dried to produce the alumina product. This allows several degrees of freedom for varying the physical properties of the final product; for instance, the amount of turbulence in the reactor and the speed of the spray dryer atomizer wheel are two of the most important design criterions.

The decision to produce alumina is based on an expected threefold increase in alumina catalyst-support demand between 1974 and 1985 (from 73.4 to 210 million pounds per year). This increased demand is expected to arise from four areas:

1. Petroleum refining catalysts
2. Resid desulfurization catalysts
3. Automobile emission reduction catalysts
4. Coal gasification catalysts

The last two types of catalysts' markets are much more uncertain so Conoco management has decided to try to avoid them. Conoco is in the process of committing 70-75 percent of the expected alumina production by long-term contracts. These contracts are "take-or-pay" type covering 1977 through 1981.

TABLE I

CATAPAL-SB SPECIFICATIONS

Chemical Composition (Weight Percent)	
Al_2O_3	70% Min. - 78% Max.
C	0.5% Max.
SiO_2	0.01% Max.
Fe_2O_3	0.01% Max.
Na_2O	0.01% Max.
Physical Properties	
Particle Size Distribution	Smaller Than 45 Microns, 55% Max.
	Greater Than 90 Microns, 15% Max.
Bulk Density, Loose	730-810 Grams Per Liter (45-51 Lbs. per Cubic Foot)
Pore Volume (0-800A)*	0.4 Milliliters Per Gram Min.
Spec. Surface Area (BET)*	230 Square Meters Per Gram Min. (Approximately 25 Football Fields Per Pound)
Crystallite Structure	Boehmite Type

*After calcination for 3 hours at 900°F

GENERAL PROCESS DESCRIPTION

Section 550 of the Lake Charles "ALFOL" Alcohol Unit provides for water hydrolysis of solvent-free aluminum alkoxide (produced in Section 425) with the formation of alumina and straight-chain alcohols containing even carbon numbers. High purity alumina, denatured ethanol, and solvent-grade butanol are recovered in this section while C_6+ alcohols are sent to Section 600 for further processing. Three processing systems are contained in Section 550:

A. Hydrolysis-Extraction System
B. Fractionation System
C. Alumina Recovery System

In the hydrolysis-extraction system, stripped aluminum alkoxide reacts with water according to the following equations:

$$\underset{\text{(Monoaluminum Alkoxide)}}{2Al(OR)_3} + 3H_2O = \underset{\text{(Alumina)}}{Al_2O_3} + 6ROH \qquad (1)$$

$$\underset{\text{(Dialuminum Alkoxide)}}{Al_2(OR)_4O} + 2H_2O = Al_2O_3 + 4ROH \qquad (2)$$

$$\underset{\text{(Titanium Alkoxide)}}{Ti(OR)_4} + 2H_2O = TiO_2 + 4ROH \qquad (3)$$

The above reactions are exothermic and carried out at 200°F in the presence of excess water. The two products from the reaction are an alumina-water slurry and crude alcohols. These are mutually insoluble and separate in the hydrolysis reactor. Any C_6+ alcohols contained in the alumina-water slurry from the hydrolysis reactor are removed in a two-stage countercurrent extraction with butanol.

In the fractionation system, the wet crude alcohol from the hydrolysis reactor is sent to a dehydrator tower where the water is removed. The condensed overheads from the dehydrator tower and the butanol stripper (in the alumina recovery system) are combined and sent to the dehydrator tower overhead accumulator. This combined stream, which consists of water, ethanol, and butanol, separates into two phases in this accumulator. The water phase is combined with makeup condensate and barometric condenser blowdown water and recycled to the hydrolysis reactor. The alcohol phase is fed to an ethanol tower where a 93 percent ethanol product is recovered. The bottoms from the ethanol tower consists of water and butanol which is used for extraction in the hydrolysis-extraction system.

The water-free crude alcohol from the dehydrator tower is sent to a butanol tower where a high purity butanol product is taken overhead. Most of the butanol product is recycled to the process while the net make butanol is sent to the hydrogenation section. The bottoms from the butanol tower is transferred to Section 600 for further fractionation.

In the alumina recovery system, the alumina-water slurry from the hydrolysis-extraction system is sent to a butanol stripper where butanol is stripped from the slurry with steam. The alcohol-free slurry is then sent to a spray dryer for recovery of a high purity, high surface area powdered alumina. The spray dryer utilizes direct heating with air and flue gases which enter at 1,400°F and exit at 300-350°F. The alumina product (75 percent alumina/25 percent water) from the spray dryer is transferred to product storage where it is loaded into railcars and trucks for bulk shipment.

DETAILED PROCESS DESCRIPTION

A. Hydrolysis-Extraction System

Stripped aluminum alkoxide is received from Section 425 at 160°F. The alkoxide is pumped from intermediate storage tanks FB-506A or FB-508, heated to 200°F with steam in EA-551, and injected into the hydrolysis reactor, DC-551, through a small diameter nozzle which promotes turbulence. The alkoxide enters the reactor in the slurry phase between the two impellers of the reactor mixer. It reacts rapidly to form crude "ALFOL" alcohols and hydrated alumina.

The hydrolysis water to the reactor consists of makeup condensate, barometric condenser blowdown water, recycle water from the distillation system, and ammonium hydroxide solution from the ammonia absorber. Condensate is used as process water to prevent contamination of product alumina with foreign minerals. The hydrolysis water is pumped from the hydrolysis water tank, FB-551, to the hydrolysis reactor, DC-551, via the steam ring heater, PA-551. In this heater, the water temperature is raised to about 170°F by direct steam injection.

An ammonia concentration of about 0.15 weight percent is maintained in the hydrolysis water. The ammonia prevents formation of emulsions in downstream equipment. This concentration is maintained by injection of ammonium hydroxide into this stream intermittently.

A wet butanol stream from the extraction system also enters the slurry phase of the reactor to enhance removal of heavier alcohols.

A crude alcohol phase and an alumina-water slurry phase are produced in the hydrolysis reaction. A nitrogen pressure of 80 psig is maintained in the hydrolysis reactor to permit transfer of slurry by pressurization rather than pumping. In normal operation, most of the crude alcohol is pressured directly from the reactor to the dehydrator tower to conserve energy. The remaining alcohol is cooled in EA-553 to 175°F and sent to the alcohol surge tank, FB-553. Five recycle alcohol streams also flow into this tank:

1. Remelted barometric condenser cooling tower sump scrapings

2. Remelted railcar scrapings

3. '6' tower overheads from Section 600

4. Off-spec. alcohols from Section 600

5. Skimmed alcohols from hydrolysis water tank, FB-551

These alcohols are pumped from FB-553 to the dehydrator tower continuously during normal operation.

The alumina-water slurry phase from the hydrolysis reactor contains dissolved and entrained alcohols. The alcohols must be removed and recovered to avoid an unacceptable carbon content in the alumina product and avert an alcohol product loss.

A two-stage countercurrent extraction with butanol is used to remove the C_6+ alcohols from the slurry. The alumina slurry is pressured from the hydrolysis reactor, DC-551, to the first stage mixing drum, FA-553. Here, contact is made with the butanol phase from the second stage phase separator drum, FA-554. The effluent from the first stage mixer is phase split in the first stage phase separator drum, FA-552. The alcohol phase from FA-552 is pumped to the hydrolysis reactor.

The alumina slurry from the first stage phase separator is pressured to the second stage mixing drum, FA-551. Here it contacts fresh recycle butanol from the recycle butanol tank, FB-552. In order to maintain the alumina slurry at 185°F, the recycle butanol is preheated to 169°F in EA-552. The alcohol/slurry mixture from the second stage mixer is transferred to the second stage phase separator, FA-554. The alcohol phase from this separator is pumped to the first stage mixing drum. The slurry is pressured to the butanol stripper, DA-554.

Parameters effecting the operation of the reaction-extraction system are reaction and extraction temperatures, hydrolysis water and recycle butanol flow rates, and ammonia and ethanol concentration. The most economical operation is at the following conditions:

1. Minimum Hydrolysis Water Flow (or Maximum Slurry Concentration)--since the water in the slurry is evaporated during spray drying, less water results in less condensate makeup and fuel requirements.

2. Minimum Butanol Recycle Flow--since less butanol decreases the load on the fractionation system.

Hydrolysis water flow rate should be set to give a butanol stripper slurry feed concentration of 9-12 weight percent solids; higher solids concentrations can cause slurry transfer problems. Recycle butanol flow rate should be set at the minimum value which consistently gives acceptable extraction. The design hydrolysis reaction temperature is 200°F. Higher temperatures will decrease alumina product surface area and increase butanol solubility in the slurry. The reaction temperature is regulated by adjusting hydrolysis water and alkoxide feed temperatures. Temperature of the second stage extraction is set based on butanol solubility in the slurry and slurry flow characteristics. Emulsions can occur in the reaction-extraction system due to ammonia deficiencies or excess ethanol concentrations. The ethanol tower removes the net make ethanol and is designed to give minimum ethanol recycle.

B. Fractionation System

Crude alcohol containing approximately 11 weight percent water is fed to the dehydrator tower, DA-551, directly from the reactor, DC-551, and from the alcohol surge tank, FB-553. Before entering the tower, the feed is filtered in FD-551 to remove any entrained alumina particles and then heated to its bubble point of 208°F in EA-555. The dehydrator removes the water, as a butanol/water azeotrope, along with the ethanol and ammonia. High purity butanol from the butanol tower is "refluxed" to the top tray of the tower to minimize C_6+ alcohol carryover.

The water-free crude alcohol bottoms from the dehydrator tower is fed to the butanol tower, DA-553. A 99+ percent butanol product is distilled overhead in the butanol tower. The butanol tower overhead product provides reflux to the dehydrator tower and supplements the recycle butanol requirements (to the hydrolysis-extraction system). The net make butanol is sent to the hydrogenation section. The butanol-free tower bottoms is transferred to intermediate storage located in Section 600.

The dehydrator tower overhead is condensed, subcooled to 160°F, and combined with the butanol stripper overhead (also at 160°F). The combined stream enters the dehydrator tower overhead accumulator, FA-555, and separates into an alcohol phase and an aqueous phase. The aqueous phase is pumped to the steam ring heater, PA-551, for recycle to the hydrolysis reactor.

The alcohol phase from the dehydrator tower overhead accumulator is fed to the ethanol tower, DA-552. The ethanol tower removes the net make ethanol and minimizes ethanol recycle to the hydrolysis-extraction system. Low ethanol recycle rates reduce emulsion formation in the hydrolysis reactor. The ethanol product is removed as an ethanol/water azeotrope (about 93 weight percent ethanol) from a sidedraw on tray 11 of the ethanol column. The ethanol sidedraw product gravity flows to product storage FB-506C. The top ten trays of the ethanol tower remove ammonia from the ethanol product. The overhead vapor consisting of most of the ethanol and water and essentially all of the ammonia is partially

[illegible] feed filter, FD-552, to the spray dryer, EC-551, using another positive displacement pump with a variable-speed drive. The slurry enters the spray dryer through a centrifugal wheel atomizer. The resulting slurry droplets contact the hot air and flue gases from the spray dryer air heater, BA-551. Combined stripper overhead from Section 425 (liquid fuel) is pumped in from FB-555 to fire the heater. The inlet hot air temperature is maintained at 1,400°F by using excess air supplied by GB-551, the combustion air blower. The exhaust gases and alumina leave the spray dryer at 300-500°F and enter a baghouse, FD-555, which recovers the alumina product. The alumina-free exhaust gas is vented to the atmosphere from the spray dryer exhaust fan discharge, GB-552.

condensed in EA-560 and enters the overhead accumulator, FA-558. The liquid in FA-558 is returned as reflux to the ethanol tower. The uncondensed vapor from FA-558 is partially condensed in the ethanol tower vent condenser, EA-562, and returned by gravity flow to FA-558. The purpose of EA-562 is to minimize ethanol recycled to the hydrolysis-extraction system. The uncondensed vapor from EA-562 which is mostly ammonia with some ethanol and water, is absorbed with service water in the ammonia absorber, DA-555. The ammonium hydroxide solution gravity flows from DA-555 to the hydrolysis water tank, FB-551. This enables almost all the ammonium hydroxide introduced into the process to be recycled, minimizing fresh ammonium hydroxide makeup and pollution problems.

The ethanol tower bottoms is cooled to 150°F in EA-558 and transferred to the recycle butanol tank, FB-552.

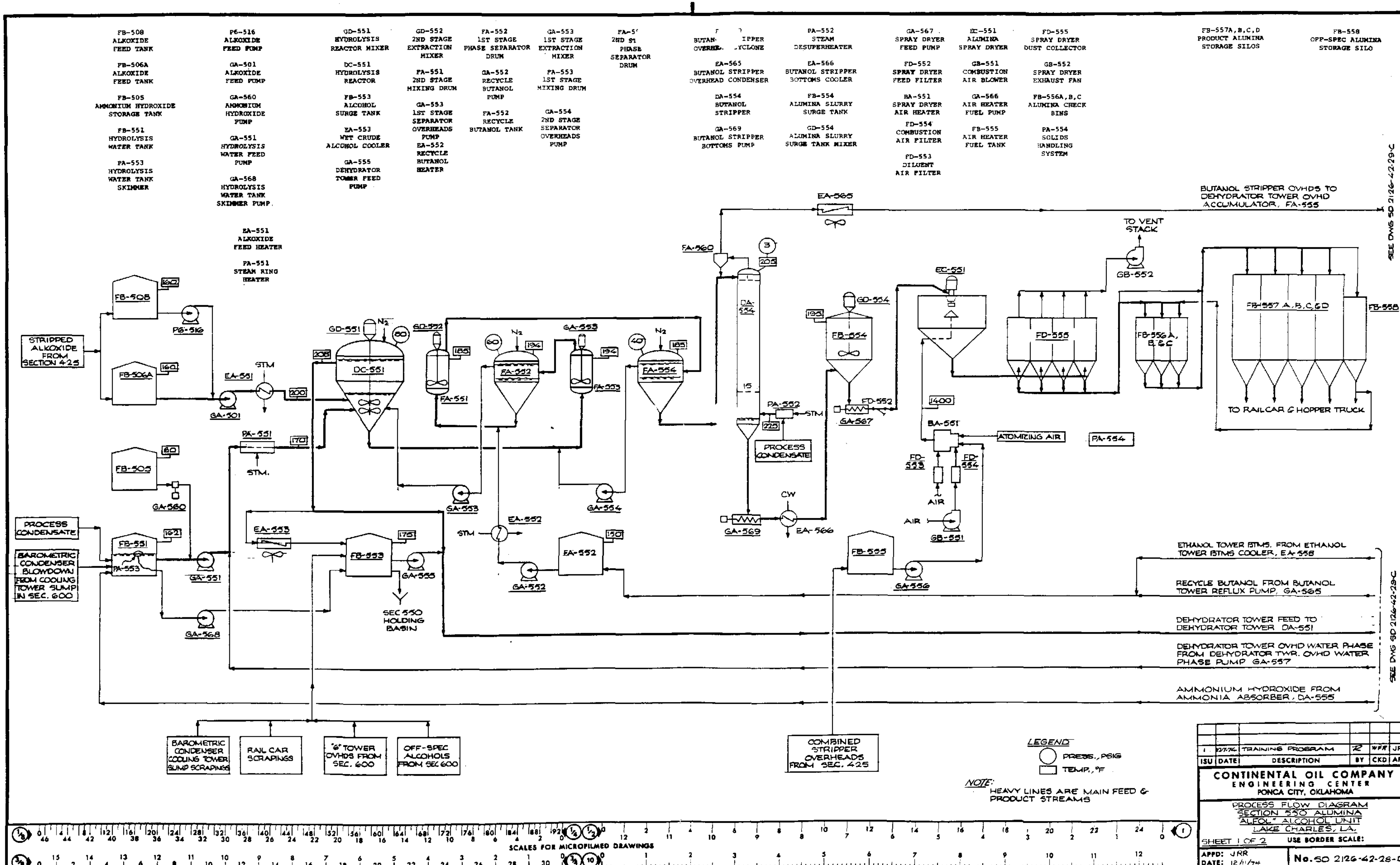
C. Alumina Recovery System

The alumina slurry from the second stage separator drum, FA-554, is pressured directly to the butanol stripper, DA-554. The slurry is fed to the top tray. Live steam, desuperheated in PA-552 to process conditions, is used to strip all butanol (as a butanol/water azeotrope) and lighter components from the slurry. A cyclone, FA-560, is provided in the butanol stripper overhead vapor stream to remove any entrained alumina particles. The overhead is condensed and subcooled to 160°F in EA-565 and combined with the dehydrator tower overhead stream (see above).

The alcohol-free slurry is pumped from the butanol stripper using a positive displacement pump with a variable-speed drive. This slurry first enters EA-566 where it is cooled to 195°F and then it flows to the alumina slurry surge tank, FB-554.

The alumina slurry is pumped from FB-554 through the spray dryer feed filter, FD-552, to the spray dryer, EC-551, using another positive displacement pump with a variable-speed drive. The slurry enters the spray dryer through a centrifugal wheel atomizer. The resulting slurry droplets contact the hot air and flue gases from the spray dryer air heater, BA-551. Combined stripper overhead from Section 425 (liquid fuel) is pumped in from FB-555 to fire the heater. The inlet hot air temperature is maintained at 1,400°F by using excess air supplied by GB-551, the combustion air blower. The exhaust gases and alumina leave the spray dryer at 300-500°F and enter a baghouse, FD-555, which recovers the alumina product. The alumina-free exhaust gas is vented to the atmosphere from the spray dryer exhaust fan discharge, GB-552.

The alumina product from the baghouse is transferred to one of the alumina check bins, FB-556A, B, and C (one for each shift). After product testing, the alumina is transferred to one of the product silos, FB-557A, B, C, and D. The product is loaded into trucks and railcars. Inventories are measured by load cells on the silos. An off-specification product silo, FB-558, is also available when needed.



4-283 S

SAI 000010385

EA-555 DEHYDRATOR TOWER FEED PREHEATER

FD-551 DEHYDRATOR TOWER FEED FILTER

GA-557 DEHYDRATOR TOWER OVERHEAD WATER PHASE PUMP

DA-551 DEHYDRATOR TOWER

EA-556 DEHYDRATOR TOWER REBOILER

GA-558 DEHYDRATOR TOWER OVHD ALCOHOL PHASE PUMP

EA-557 DEHYDRATOR TOWER OVERHEAD CONDENSER

FA-555 DEHYDRATOR TOWER OVERHEAD ACCUMULATOR

GA-556 DEHYDRATOR TOWER BOTTOMS PUMP

EA-558 ETHANOL TOWER BOTTOMS COOLER

FA-559 CONDENSATE DRUM

DA-552 ETHANOL TOWER

FA-558 ETHANOL TOWER OVHD ACCUMULATOR

EA-560 ETHANOL TO. OVHD CONDENSER

EA-559 ETHANOL TOWER REBOILER

GA-559 ETHANOL TOWER BOTTOMS PUMP

GA-561 ETHANOL TOWER REFLUX PUMP

EA-5 ETHANOL ER VENT CONDENSER

DA-555 AMMONIA ABSORBER

FB-506C ETHANOL PRODUCT TANK

EA-563 ETHANOL TOWER REBOILER

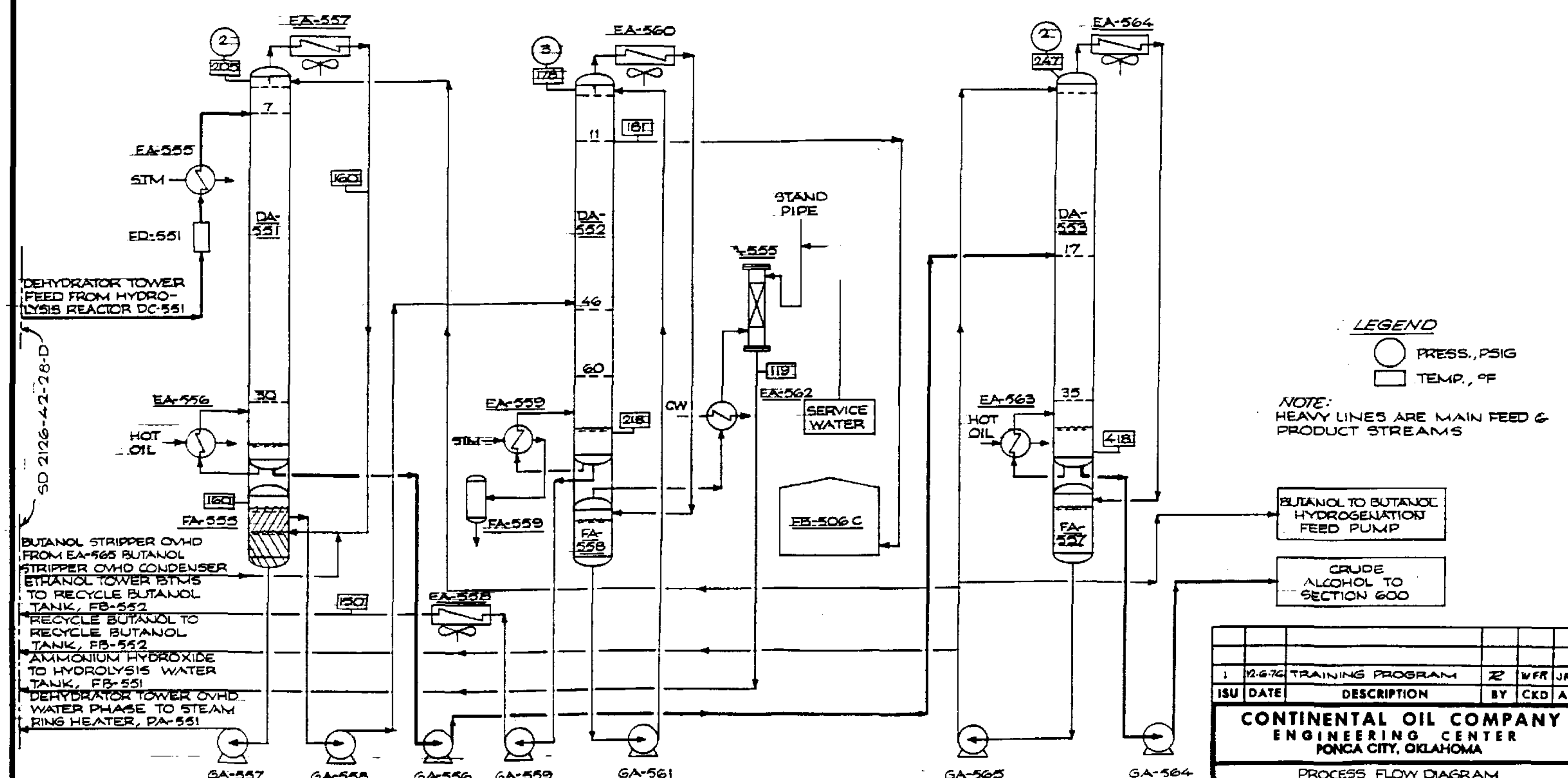
GA-565 BUTANOL TOWER REFLUX PUMP

DA-553 BUTANOL TOWER

FA-557 BUTANOL TOWER OVERHEAD ACCUMULATOR

EA-564 BUTANOL TOWER OVHD CONDENSER

GA-564 BUTANOL TOWER BOTTOMS PUMP



ISU	DATE	DESCRIPTION	BY	CKD	APD
1	12-6-76	TRAINING PROGRAM	R	WFR	JRR

CONTINENTAL OIL COMPANY
ENGINEERING CENTER
PONCA CITY, OKLAHOMA

PROCESS FLOW DIAGRAM
SECTION 550, ALUMINA
ALFOL ALCOHOL UNIT
LAKE CHARLES, LA.

SHEET 2 OF 2 USE BORDER SCALE:

APPD: JRR
DATE: 12/11/74

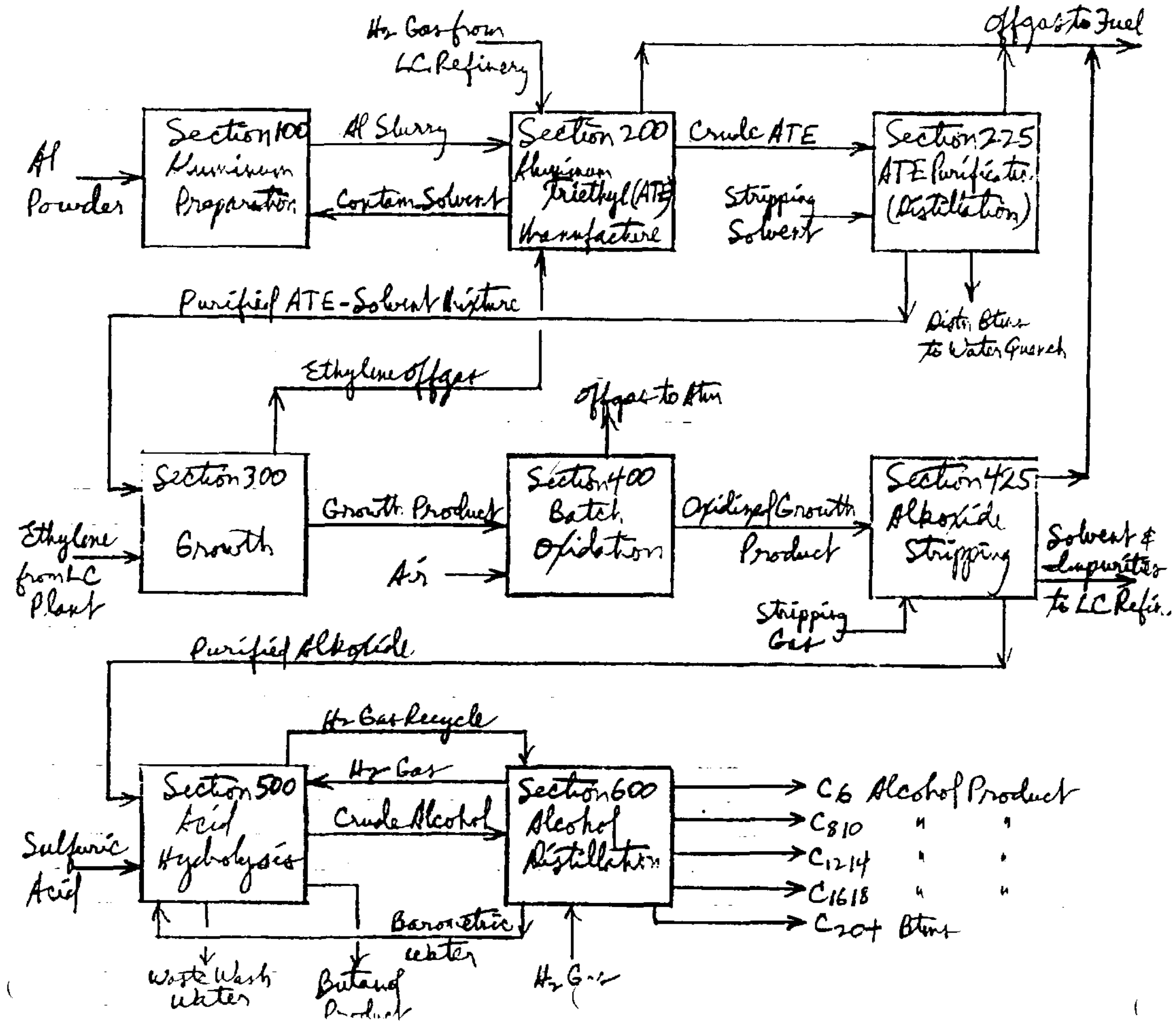
No. SD 2126-42-29-C

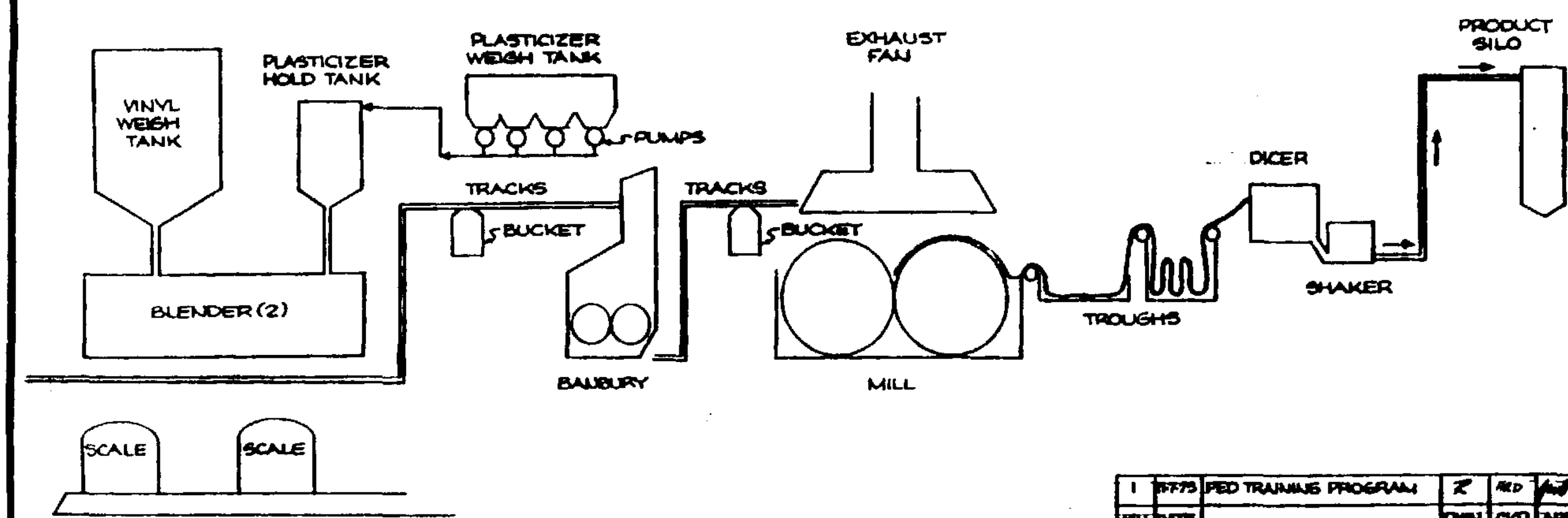
SCALES FOR MICROFILMED DRAWINGS

4-282 S

LCCP Alcohol Process

12/16/94





1	11-7-75	FED TRAINING PROGRAM		
FSU	DATE		DWN	CKD	APD

CONTINENTAL OIL COMPANY
ENGINEERING CENTER
PONCA CITY, OKLAHOMA

SIMPLIFIED PROCESS FLOW DIAGRAM
COMPOUND AREA
ABERDEEN, MISS.

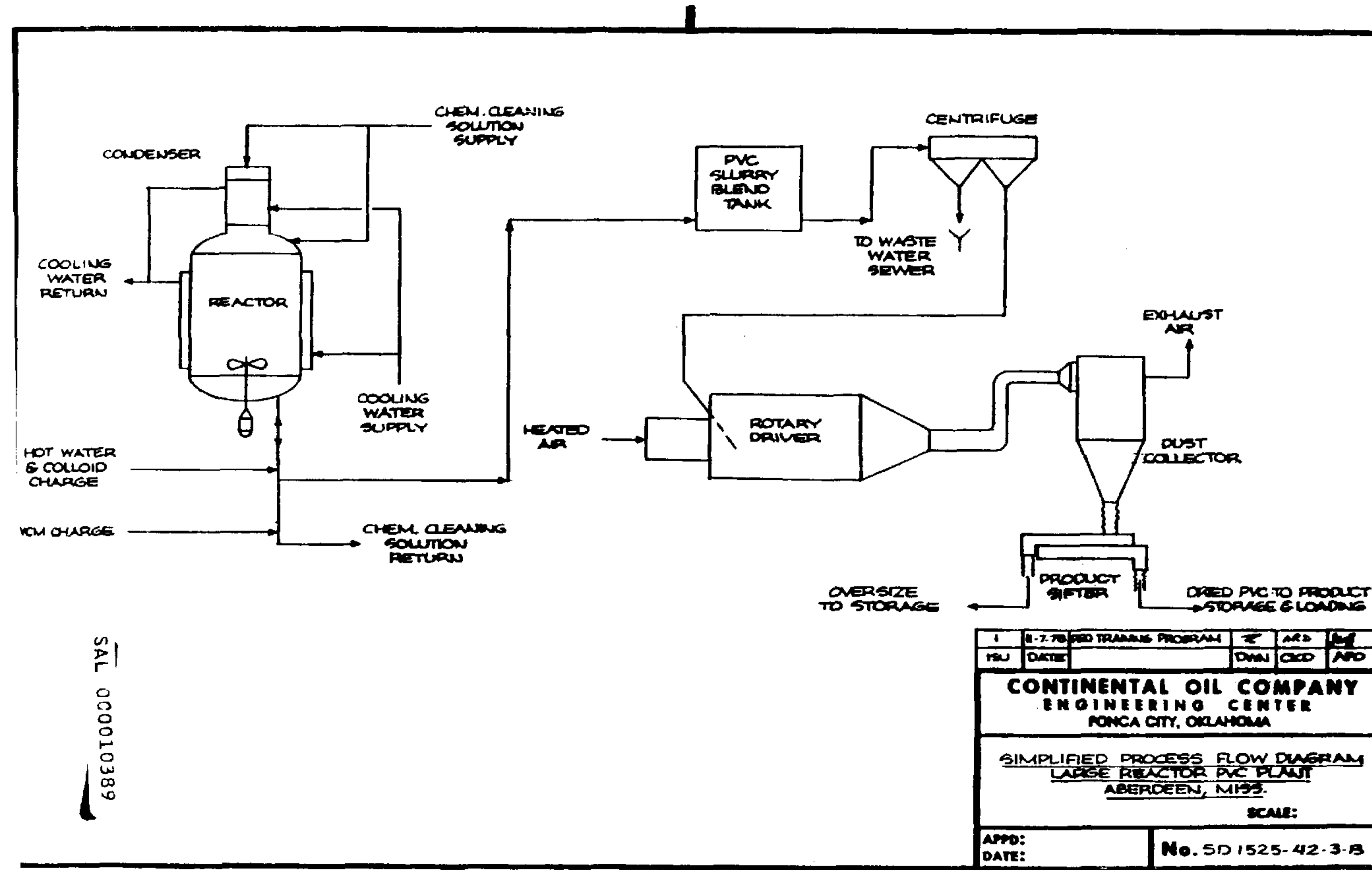
SCALE:

APPD:
DATE:

No. SD1525-42-4-B

SAL 000010388

4-281 S


CHEM. CLEANING SOLUTION SUPPLY
CONDENSER
CENTRIFUGE
PVC SLURRY BLEND TANK
COOLING WATER RETURN
REACTOR
TO WASTE WATER SEWER
EXHAUST AIR
COOLING WATER SUPPLY
HEATED AIR
ROTARY DRIVER
DUST COLLECTOR
HOT WATER & COLLOID CHARGE
VCM CHARGE
CHEM. CLEANING SOLUTION RETURN
PRODUCT SIFTER
OVERSIZE TO STORAGE
DRIED PVC TO PRODUCT STORAGE & LOADING
ISU
DATE
DWN
CKD
APD
CONTINENTAL OIL COMPANY
ENGINEERING CENTER
PONCA CITY, OKLAHOMA
SIMPLIFIED PROCESS FLOW DIAGRAM
LARGE REACTOR PVC PLANT
ABERDEEN, MISS.
SCALE:
APPD:
DATE:
No. 5D 1525-42-3-B

4-281 S