

PED ORIENTATION PROGRAM

LAB PLANT

LAKE CHARLES, LOUISIANA

Preface

The LAB plant is presently under construction and plant startup is scheduled for late 1982.

SAL 000010160

PED ORIENTATION PROGRAM

LAB PLANT

LAKE CHARLES, LOUISIANA

INTRODUCTION

The HF Detergent Alkylation Process is a catalytic process to alkylate benzene with linear olefins to form linear alkyl benzene. The linear alkylbenzenes produced from the C₁₀-C₁₃ linear olefins are useful detergent intermediates and can be readily sulfonated (treatment with oleum or sulfur trioxide and neutralization with NaOH) to yield linear alkylbenzene sulfonates. These compounds constitute the "active" ingredients of many household detergents. They are surface active compounds (surfactants) which are combined with various builders (often inorganic salts) to make up a detergent formula. (See Table I).

During the 40's and 50's, the detergent market was primarily captured by dodecylbenzene (DDB), product formed by alkylation of benzene with propylene tetramer in a hard detergent alkylation unit. It was found, however, that the branched structure of the alkyl group was responsible for the poor biodegradability of the detergent and the linear alkylbenzenes (LAB) introduced in the early 60's have substantially replaced their branched counterparts. Some of the new alkylation units are designed for the dual purpose of taking care of present markets (hard detergent) and future markets (soft detergents); they can be charged with propylene tetramer or Pacol linear olefin and yield the respective alkylbenzenes.

Sodium linear alkylbenzene sulfonate (LAS) is a high quality, safe and biodegradable detergent which is produced at competitive costs. It is one of the most important sources of detergent and the world-wide annual production of LAB was 820,000 MT in 1973 while the production of DDB was 230,000 MT during the same period.

The first unit in a detergent complex is an n-paraffin extraction unit (like the UOP Molex Unit) which extracts n-paraffins from a kerosene feed. Pure n-paraffins are then dehydrogenated in the UOP Pacol Unit and the mixture of about 12 percent n-olefins and 88 percent n-paraffins is charged to the detergent alkylation unit. The unreacted normal paraffins are continuously recycled to the Pacol feed after going through the alkylation section while the n-olefins are completely alkylated in the alkylation reactors. It was found that adjusting the Pacol reactors to about 12 weight percent olefin conversion is the most economical way to operate the units in terms of product quality and operating costs.

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PROCESS DESCRIPTION OF THE PACOL UNIT

The UOP Pacol* Process is a process to dehydrogenate high purity linear paraffins to their corresponding mono-olefins. An olefin-free stream from the process downstream of the Pacol Process is usually recycled to the Pacol Unit and combined with the fresh feed. This recycle stream may be the raffinate product from an Olex Unit, or the unreacted paraffins from an Alkylation Unit.

The Pacol Process Unit consists of a catalytic, fixed-bed reactor wherein a portion of the combined linear paraffin feed is dehydrogenated to the corresponding mono-olefins. The reaction is carried out in the presence of hydrogen at low pressure and moderately high temperatures. The feed to the downstream unit is from the product stripper in which light ends and water are taken overhead.

PACOL UNIT PROCESS VARIABLES

Reactions

As is true with other hydrogen-producing processes, the Pacol reactor outlet temperature will be lower than the inlet. The reactor conditions are adjusted to maintain a total linear olefin concentration in the reactor separator liquid effluent of about 11.0-12.5 weight percent, depending on the design factors for each particular unit. The selectivities are such that about 90 percent of the converted linear paraffins are mono-olefins. The remaining ten percent are mainly di-olefins and aromatics with lesser amounts of light ends, iso-paraffins and iso-olefins. The gas produced by the dehydrogenation reactor is a hydrogen-rich gas ranging from 99 to 76 mol percent H_2 over the length of the run. The double bond of the product mono-olefins is randomly distributed along the chain, with about ten percent in the alpha position.

There is no difficulty in operating at a lower total normal olefin concentration than design. Higher concentrations, however, should be avoided because of the excessive amounts of aromatics that would be formed.

At a given temperature, the lower carbon number hydrocarbons in each class are less reactive than the higher carbon number hydrocarbons of the same class. Naphthenes have a lower reactivity than any of the paraffins. The aromatics are essentially non-reactive, except for the small amount that may be hydrocracked. Thus, on startup and following each change in conversion rate in the reactor, the equilibrium concentrations will shift. When the conversion rate is increased, the recycle paraffin stream will slowly become enriched with the lower carbon number paraffins. As the conversion rate is decreased, the recycle stream will become enriched with the higher carbon number paraffins, with the resulting reduction in the lower carbon number paraffins.

*Registered Trademark

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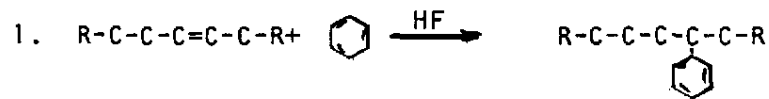
PROCESS DESCRIPTION OF THE SOFT DETERGENT ALKYLATION UNIT (CONTINUED)

Effluent Control

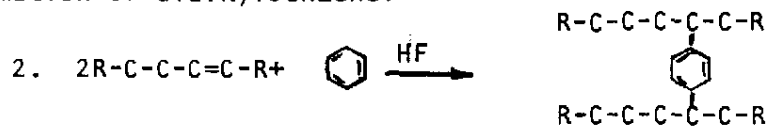
Hydrofluoric acid handling and disposal is a delicate operation and the plant is designed with safety of both equipment and personnel as a major objective. All effluents containing acid or trace acid are treated before leaving the unit.

Some Chemistry

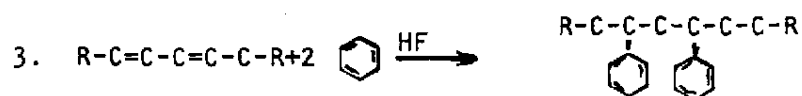
The main reaction is the alkylation of benzene with the straight chain olefins to yield a linear alkylbenzene:



At the existing conditions, some side reactions take place like the formation of dialkylbenzene.



or the formation of diphenylalkanes



or the formation of heavier components by combination of the above reactions.

Quality Control of the Products

The most desired product is the linear alkylbenzene described in reaction 1 and the unit is operated such that more than 90 percent of the crude alkylate produced will be LAB. The linear alkylbenzene is fractionated from the heavy alkylates in the rerun column, where one can adjust the split to get the desired product purity. Typically, the rerun column overhead will contain about 97 percent alkylbenzene with 3 percent indans and tetralins and 94 percent of linear alkyl benzene (see Table II). The rerun column bottoms will contain five to twenty percent LAB, 30 to 40 percent dialkylbenzenes, 30 to 40 percent diphenylalkane and other heavier components.

The linear olefins produced in the Pacol Unit are a mixture of the various isomers in similar proportion except for the olefins which are less than ten percent of the total isomers. (In the case of a chain of even carbon number, the olefin with the double bond in the central position will be in lower concentration because there is only one possibility to generate it.)

PROCESS DESCRIPTION OF THE SOFT DETERGENT ALKYLATION UNIT (CONTINUED)

Quality Control of the Products (Continued)

The alkylation reaction will respect the above distribution, except that the 1 phenyl-n alkane will not exist. Because of the lower content of alpha olefins, the 2 phenyl n-alkane will exist in lower proportion but all the other isomers will be about equally distributed.

Because of the higher foaming properties of the 2 phenyl alkane, some customers will require upper limits in its concentration and the UOP detergent process will meet them because of the preceding considerations. It should also be noted that because the Pacol process produces pure normal olefins with little branched chain olefins, the detergent alkylate produced has excellent biodegradability and compares favorably with the competition's detergent quality.

Another important quality control element is the Bromine Index of the LAB product which is an indication of the degree of unsaturation and condensed aromatic rings. Since these components will discolor the sulfonated LAB, a maximum bromine index of ten to twenty is usually specified for the LAB product. The olefins and polyaromatic compounds dissolve to some extent in HF and will be removed as HF regenerator bottoms as long as HF acid is not saturated with aromatics. The Bromine Index of the LAB is usually a function of the efficiency of the regeneration in the HF regenerator. The Bromine Index of the overhead product is also a function of the split performed in the rerun column.

The di-alkylbenzene component of the heavy alkylates produced from the bottom of the rerun column have been used to produce lube oil detergents. Their color is an important specification and usually is directly related to the performance of the HF regenerator. The viscosity must also be kept high to be used as lube oil additives.

ALKYLATION UNIT PROCESS VARIABLES

HF/Hydrocarbon

Most units are designed with an HF to hydrocarbon volume ratio of two. This normally provides sufficient acid to obtain the expected yield structure and product quality. Increasing the ratio should theoretically improve the yield structure but this effect has not been conclusively observed in commercial units. Most commercial units operate at HF/HCBN ratios of 1.5 to 2.0, and the lower ratios have been obtained at higher than design throughputs which probably improved the mixing. Reducing the HF circulation does not significantly affect the utilities consumption; it does, however, tend to increase the bromine index of the final product.

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ALKYLATION UNIT PROCESS VARIABLES (CONTINUED)

Benzene/Olefin

Most units are designed with a benzene to olefin mol ratio of ten. This normally provides enough olefin dilution to obtain the expected yield structure.

Above a ratio of ten, however, the improvement is usually insignificant. Decreasing the ratio increases the formation of di-alkylbenzene and heavy alkylate. Most commercial units operate with a benzene/olefin ratio between five and twelve. The lower ratios generally produce a yield structure that would not meet a typical UOP guarantee.

Reducing the benzene circulation saves a large amount of heat because all the circulated benzene is a fractionator overhead product. Some trade-off in lower yield for lower utilities may be economically justified in most plants.

Temperature

The reactors are usually operated around 100°F. Since the soft detergent is more thermally stable than the hard detergent, the temperature of the second reactor can sometimes be increased to 140°F to eliminate the last traces of olefins. However, the reaction is very rapid and is usually complete in the first reactor; so the observed effect of temperature is minimal.

Pressure

The pressure has essentially no effect on the reaction. It should be kept high enough to keep all components in the liquid phase.

HF Regenerator Feed/LAB Product

HF has the property to selectively extract some heavy aromatic byproducts of the alkylation reaction which would otherwise wind up in the finished products. The HF regenerator is the recovery column of this extraction process, where pure solvent is recovered in the column overhead and the extract (in this case, the heavy polyaromatics) found in the column bottom.

This extraction can be viewed as a two-stage, countercurrent extraction, the two stages corresponding to the two reactors. To set up this countercurrent system, the regenerated acid from the regenerator overhead is directed to the inlet of the second-stage reactor while a slipstream of acid from the second-stage settler is recycled to the first-stage reactor. To complete the loop, a slipstream of acid from the first-stage system is fed to the HF regenerator. To maintain a constant acid inventory in both first and second stages, the three flows described above are equal.

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ALKYLATION UNIT PROCESS VARIABLES (CONTINUED)

HF Regenerator Feed/LAB Product (Continued)

The extent of this circulation determines the purity of the HF. As in any solvent system, higher extract loads in the solvent reduce the effectiveness of the solvent. Thus, the purer the acid, the better the alkylate quality. These polyaromatics (improperly called polymers) found in the HF regenerator bottoms are highly unsaturated compounds which would otherwise wind up in the rerun column both in the overhead product and in the bottom product.

In the overhead they will increase the bromine index of the LAB, and in the bottom they will color the heavy alkylates beyond acceptable specifications. One way to characterize these unsaturated compounds is to assign them a "J" number. The "J" number of a product is a measure of the degree of unsaturation of this product. For example, the "J" number of benzene is 6. These "polymers" have a "J" number as high as "J=18".

If the HF regenerator performs satisfactorily, the amount of feed fed to it will determine the purity of the circulating HF. This number is usually logged in as HF regenerator feed/LAB product, and is usually around 0.5 to 1. It is a very important parameter to control the quality of the final products.

If the acid is saturated with polyaromatics, its color will be dark. The color of the acid is a good indication of its purity - the lighter the color, the purer the acid. The color of the acid can range anywhere between almost white to dark brown and can take all the shades of yellow and brown. Looking at the acid color in the HF regenerator overhead receiver, one can tell immediately if the regenerator is functioning well. The purity of the circulation acid is usually maintained above 95 percent, with about .5 percent residual water and the rest heavy hydrocarbons.

Another feature of the HF regenerator is that it removes all water present in the system. In a distillation column, water and hydrofluoric acid form an azeotrope containing about 40 percent acid and 60 percent water. This azeotrope is normally called CBM (constant boiling mixture) because of its obvious properties. Any water present in the system will come off the regenerator bottoms in the form of CBM. The HF regenerator bottoms will be drained batchwise to a polymer surge drum where CBM will separate from the hydrocarbon phase. CBM is a very corrosive substance and will corrode much more readily than pure HF. It is to be noted that in normal circumstances the production of CBM should be minimal since there is very little water entering the system; the n-paraffins are being stripped in the Pacol stripper and the benzene is dried in the benzene drying column. Any excessive CBM made is the result of a faulty operation, most probably a leak somewhere in the startup. Because of the corrosive properties of CBM, any excessive CBM formation should be checked by closely monitoring the water entering the system. The regenerator will eventually move the water, but it is not specifically designed to separate water from HF by distillation; and, in any case, elimination of a given volume of water will cause a loss of HF of almost the same amount.

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ALKYLATION UNIT PROCESS VARIABLES (CONTINUED)

Water Injection

Water is not a true variable because it does not affect yields or rates. The acid settlers are designed to separate the acid and hydrocarbon phases when the water content of the acid is about 0.3 weight percent. Increasing the water above 0.5 weight percent will increase the corrosion rates in the HF section. Reducing the water below 0.1 weight percent will increase the time required to separate the acid from the hydrocarbon and create an emulsion. At extremely low water contents, the HF-hydrocarbon mixture will require about one week to separate.

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TABLE I

STANDARD ANIONIC SURFACTANT FORMULATION

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<u>Components</u>	<u>Weight,</u> <u>%</u>
Sodium Alkylbenzene Sulfonate	20
Sodium Tripolyphosphate	40
Sodium Sulfate	34
Sodium Silicate	5
Carboxymethylcellulose	1

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TABLE II

TYPICAL PROPERTIES OF LINEAR DETERGENT ALKYLATE

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Bromine Number	0.01
Saybolt Color	+30
Unsulphonatable Content, Weight, %	1.0
Alkylbenzene Content, Weight, %	97.4
Normal Alkylbenzene, Weight, %	94.0
Biodegradability, %	
ASTM D 2667	98.1
O.E.C.D.	95.4
2-Phenyl Isomer, Weight, %	20.0
Paraffin, Weight, %	0.1
Saybolt Color of the Sodium	
Alkylbenzene Sulfonate	+26
Water, Weight, %	0.01
Doctor Test	Negative
Average Molecular Weight	240
Specific Gravity at 15.5°C	0.8612
Refractive Index, N _D 20	1.4837
Flash Point (ASTM D 93), °C	138
Distillation (ASTM D 86), °C	
IBP	281
10 Vol, %	286
30 Vol, %	288
50 Vol, %	290
70 Vol, %	293
90 Vol, %	298
95 Vol, %	302
EP	309

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NALKYLENE 550L LINEAR DETERGENT ALKYLATE
TENTATIVE SPECIFICATIONS

Properties	Specification	Typical	Test Method
Alkylate Homolog Dist. wt. %			1.090
C ₁₀	5-15	8.1	
C ₁₁	—	27.9	
C ₁₀ + C ₁₁	30-50	36.0	
C ₁₂	—	37.7	
C ₁₃	—	25.8	
C ₁₄	10 max	0.5	
C ₁₃ + C ₁₄	30 max	26.3	
C ₁₅ + higher	2 max	0.5	
2-Phenyl isomer, wt. %	12-22	17.0	1.090
Total Material < C ₁₀ LAB, wt. %	0.5 max	0.2	1.090
Average Molecular Weight	240-248	242	1.090
Bromine Number	0.01 max	<0.01	ASTM D 2710-72
Saybolt Color	29 min	30 +	1.011
Completeness of Sulfonation, %	98 min	98.5	1.059
Doctor Test	Negative	Negative	ASTM D-484
Specific Gravity (60°F/60°F)	0.860-0.870	0.8620	1.023
Water, wt. %	0.1 max	0.004	1.016
Color of Na Sulfonate, Klett (5% Al)(oleum)	60 max	50	1.042
Biodegradability	Must pass	Pass	SDA Test

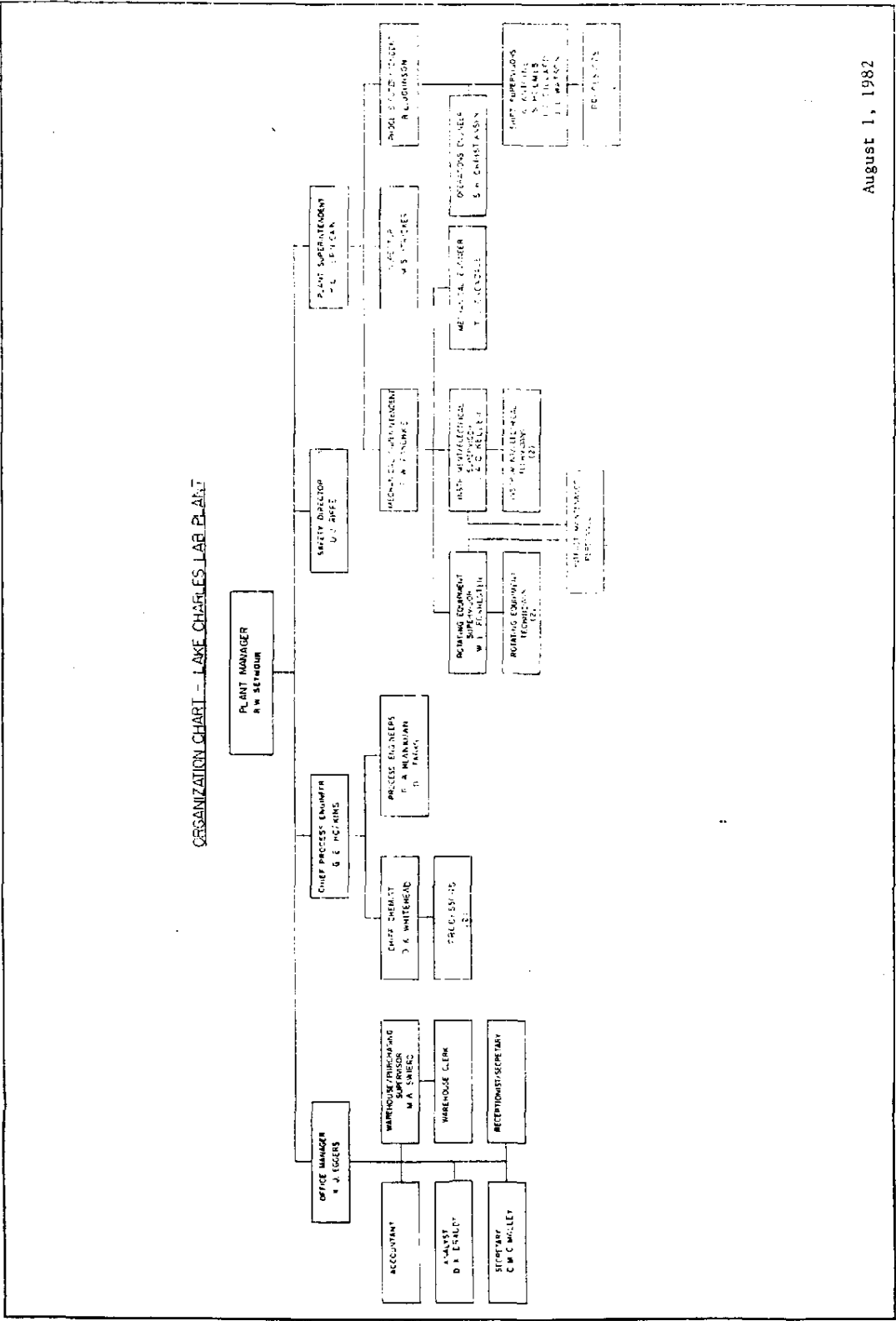


NALKYLENE 600L LINEAR DETERGENT ALKYLATE
TENTATIVE SPECIFICATIONS

Properties	Specification	Typical	Test Method
Homolog Distribution, Wt.%			1.090
C ₁₀	2 max	nil	
C ₁₁	—	0.2	
C ₁₀ + C ₁₁	5 max	0.2	
C ₁₂	—	14.2	
C ₁₃	—	51.1	
C ₁₄	45 max	31.3	
C ₁₃ + C ₁₄	70-90	82.4	
C ₁₅ + higher	5 max	3.2	
2-Phenyl Isomer, Wt.%	10-20	15.0	1.090
Total Material < C ₁₀ LAB, Wt.%	0.5 max	0.1	1.090
Average Molecular Weight	258-266	263	1.090
Bromine Number	0.01 max	<0.01	1.091
Saybolt Color	29 min	30 +	1.011
Completeness of Sulfonation, %	97.5 min	98	1.059
Doctor Test	Negative	Negative	ASTM D-484
Specific Gravity (60°F/60°F)	0.858-0.868	0.8600	1.023
Water, Wt.%	0.1 max	0.004	1.016
Color of Na Sulfonate, Klett (5% Al)(oleum)	90 max	75	1.042
Biodegradability	Must pass	Pass	SDA Test

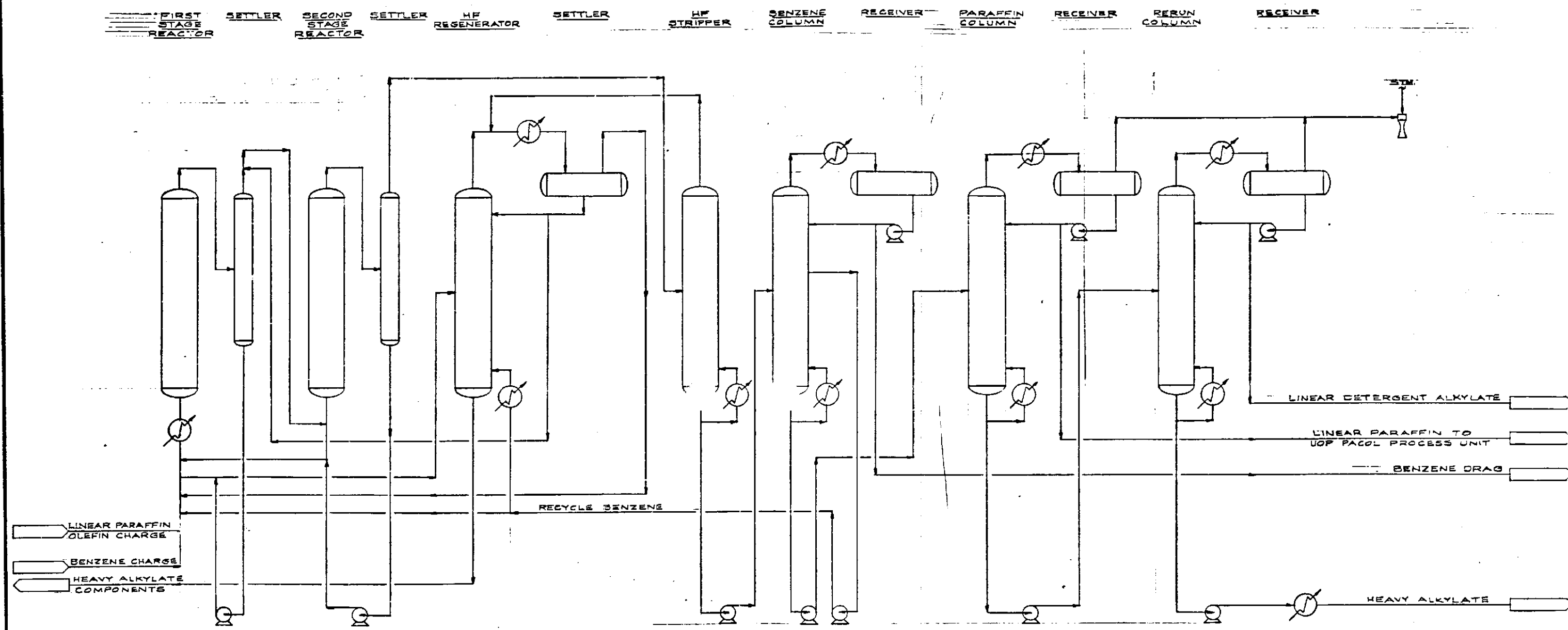
Revision 06-01-82

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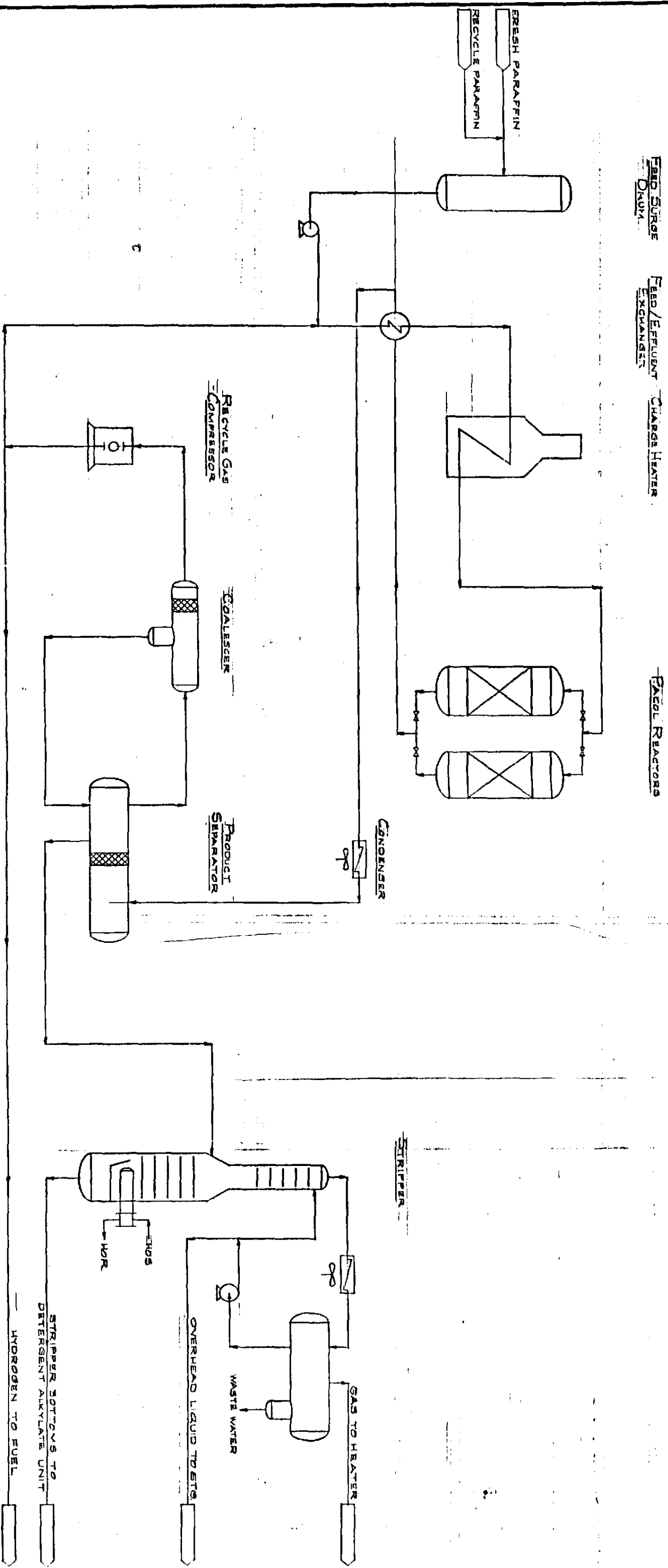
August 1, 1982

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1. PROJECT PROGRAM		2. DATE	
3. ISSUED	4. DATE	5. DESCRIPTION	6. BY
Conoco Inc. Engineering Center Ponca City, Oklahoma			
FIGURE 1 LINEAR DETERGENT ALKYLATE PROCESS			
Appd. [Signature] 11-54-54			



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PROCESS FLOW DIAGRAM

PAGE 1 OF 1

Conoco Inc.
Engineering Center
Poncha City, Oklahoma