ALKYLATED

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Continuous Pilot Plant Alkylation Reactor with 1-Inch-Diameter Packed Column

THE search for more efficient antioxidants for petroleum fractions has led many investigators to consider the alkylated phenols. The general reaction between phenols and olefins has been known for a considerable period. Many earlier investigators made and identified monoalkyl and dialkyl phenols which, in contrast to most of the trialkyl derivatives, are soluble in dilute caustic soda solution. Not, however, until about ten years ago was a systematic study started on the reactions and reaction conditions leading to the formation of trialkylated phenols. The literature covering these developments has been adequately reviewed to 1937 (1), and the fundamentals upon which the process development studies reported here are based are the subject of a series of papers now being prepared by D. R. Stevens of Mellon Institute and by G. H. Stillson of this laboratory. From this work has emerged a new class of organic chemicals, the trialkylated phenols, which are finding an ever-widening scope of usefulness.

The unique properties of these phenols, of which alkali insolubility is but one example, result primarily from the reduced activity of the phenolic hydroxyl group occasioned by the substituent alkyl groups. Stevens and Gruse (3) show the powerful antioxidant effect of certain of the trisubstituted phenols in petroleum fractions. More recently Garvey and Sarback (2) reported that dibutyl m-cresol is one of the best softeners for compounding certain types of synthetic rubber. Phenols of this class are quite soluble in petroleum fractions and in most organic solvents. The majority of these derivatives are colorless crystalline solids when freshly prepared. Discoloration, which takes place on standing, does not affect
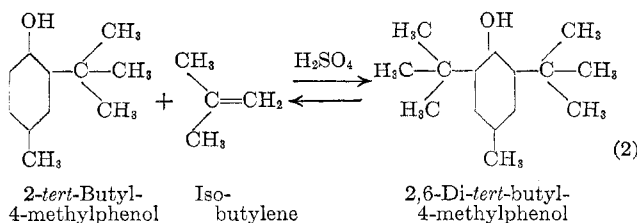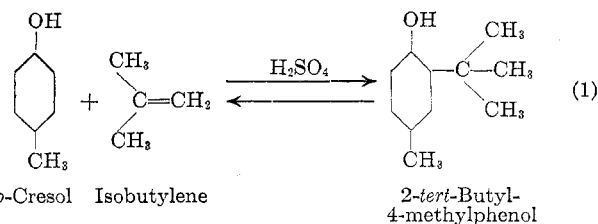
their value as oxidation inhibitors. A further distinction of the trisubstituted phenols from the parent compounds is a complete absence of burning action on the skin. Breathing of the vapors, while somewhat disagreeable, has never resulted in ill effects even to men who have operated the semicommercial plant over a period of years.

Trialkylated phenols may be obtained by treating phenols with an excess of tert-olefins in the presence of strong acid catalysts. Most investigators have described batch operations using pure olefins for these syntheses. Such processes result in good yields, but the highly concentrated olefins are relatively expensive as compared with the more dilute forms so readily available from petroleum cracking operations. Good yields of the desired products may be obtained from these less concentrated cuts, despite the diluent effect of unreactive paraffins and olefins, if the reaction is carried out in the vapor phase under proper conditions of temperature, pressure, and catalyst concentration. The development of these conditions for alkylations with dilute isobutylene streams constitutes a major portion of the work reported in this paper.

Alkylation Reactions

If a refinery butane-butene fraction is substituted for pure isobutylene, p-cresol reacts selectively with the isobutylene of the fraction when the correct reaction conditions are chosen to form the identical alkylated products. The two reversible reactions in this alkylation are cited below as typical examples of the general reactions of tertiary olefins and phenols:

$$
\begin{array}{ccc}
\text{OH} & & \text{OH} \quad \text{CH}_3 \\
\bigcirc & + \; \underset{\overset{|}{\text{CH}_3}}{\overset{\text{CH}_3}{\text{C}}}=\text{CH}_2 \;\; \xrightarrow{\text{H}_2\text{SO}_4} \; & \bigcirc\!-\!\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} \\
\text{CH}_3 & & \text{CH}_3
\end{array} \quad (1)
$$

p-Cresol   Isobutylene   2-tert-Butyl-
                                4-methylphenol

$$
(2)
$$

2-tert-Butyl-   Iso-   2,6-Di-tert-butyl-
4-methylphenol   butylene   4-methylphenol

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CRESOLS from REFINERY GASES

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The corresponding derivatives for m-cresol are 4-$tert$-butyl-3-methylphenol and 4,6-dibutyl-3-methylphenol. Only one monobutyl derivative is formed by m-cresol and by p-cresol, and evidence not yet published indicates clearly the structural formulas given above. o-Cresol, on the other hand, forms the two monobutyl isomers indicated in Table II.

In practice, the monobutylation of cresols proceeds almost quantitively to the right; only traces of cresols are left when correct alkylation conditions are employed. The equilibrium between monobutyl and dibutyl p-cresol is approximately in the molal ratio of 1:9, but for m-cresol the ratio, 2:8, is somewhat less favorable to dibutylation. When proper conditions for alkylation are chosen, these equilibriums may be reached either with pure isobutylene or with a butane-

▶ ▶ ▶ Phenols react selectively with the isobutylene contained in refinery butane-butene fractions in the presence of catalytic amounts of concentrated sulfuric acid to form the corresponding $tert$-butyl derivatives. Conditions have been determined for the synthesis of 2,6-di-$tert$-butyl-4-methylphenol and of 4,6-di-$tert$-butyl-3-methylphenol from a commercial m-p-cresol cut of coal tar acids, and continuous separation of the dibutyl cresols by distillation has been accomplished.

Early pilot plant work on this problem is briefly sketched and is followed by a more complete description of a small commercial plant for the manufacture of the $tert$-butyl derivatives of m- and p-cresol. The presence of minor proportions of o-cresol and of low-boiling xylenols in the cresol cut charged to the process introduces certain purification problems which are discussed in the light of the properties of the alkylated phenols involved.

butene fraction. It is interesting to note that when a m-p-cresol fraction of 60:40 molal ratio is charged to an alkylation reaction, the resulting monobutyl cut contains the alkylated isomers in the molal ratio of approximately 85:15.

The paraffins and n-butenes present in the refinery gases exert no detectable influence on the alkylation reaction; but a very minor proportion of the n-butenes does react with the sulfuric acid catalyst to form esters, at least part of which are suspected of being mono- and di-sec-butyl sulfates. Although acid monobutyl esters are quickly removed by washing the

alkylate with dilute caustic solution, the neutral alkylate-soluble diesters such as dibutyl sulfate must be hydrolyzed by prolonged heating of the alkylate in the presence of dilute caustic solution at temperatures above 100° C. (212° F.). If these neutral esters are not removed prior to distillation of the alkylate, they will decompose to acidic bodies causing rapid dealkylation of the alkylate.

To utilize a commercial m-p-cresol fraction, it is necessary for economic reasons that some means be available to separate the monobutyl cresols from the dibutyl cresols and to separate dibutyl p-cresol from dibutyl m-cresol. Separation by distillation of the cresols from the monobutyl cresols and of the monobutyl from the dibutyl isomers is relatively easy because of boiling point spreads of 24° C. (43.2° F.) and 20° C. (36° F.), respectively. The cresols themselves, however, boil less than 1° C. (1.8° F.) apart, and the monobutyl isomers boil only 3° C. (5.4° F.) apart. The important discovery, which cannot be predicted from previous knowledge, was made by Stevens and Livingstone (4) that the dibutyl cresol isomers boil approximately 20° C. (36° F.) apart; thus they can also be separated by distillation. The above investigators appreciated as well that this process could be applied as a means of separating p-cresol from m-cresol by the dealkylation separately of dibutyl p-cresol and dibutyl m-cresol.

Pilot Plant Investigations

The present work comprises: (a) a description of the equipment used in early batch reactions using pure isobutylene and p-cresol and in the continuous packed-tower and bubble-cap reaction systems for contacting a refinery butane-butene fraction with 3° C. (5.4° F.) commercial m-p-cresol charge stock; (b) the establishment of reaction conditions for both the batch and the continuous operations including the washing procedure necessary to free the alkylate from acid-forming by-products that must be removed prior to distillation; and (c) the separation of the alkylated cresols by distillation with a discussion of the effect on the purity of the main products by other phenols present in small quantities in the commercial cresylic acids. It was during this period that the design of the bubble-cap alkylation reactors was set and the arrangement and flow of the continuous alkylate washing and distillation systems were determined. The operating semicommercial plant is described later, with a product balance on the complete operation. This development makes available for the first time sizable quantities of alkylated cresols. Among them are monobutyl m-cresol and dibutyl m-cresol.

Batch Alkylation Experiments

The early pilot plant studies involved the preparation in large laboratory quantities of 2,6-di-$tert$-butyl-4-methylphenol from pure isobutylene and p-cresol. The necessary quantities of isobutylene were made by dehydrating $tert$-butanol at about 625° F. over activated alumina under
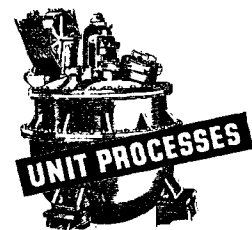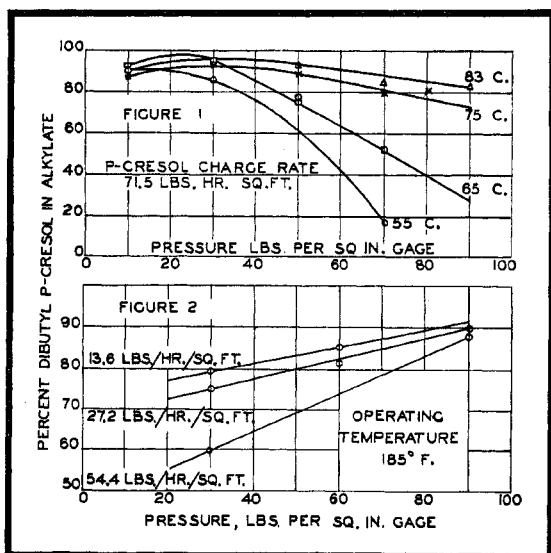
Figure 1. Effect of Pressure on Alkylation of p-Cresol in a 1-Inch Packed Tower at Various Operating Temperatures

Figure 2. Effect of Pressure on Alkylation of p-Cresol in a 4-Inch Bubble-Cap Tower for Varying Rates of p-Cresol Charge

sufficient pressure to condense both the water and the isobutylene formed. Only a trace of alcohol remained in the water layer. Alkylation was carried out at atmospheric pressure or slightly above and at 60-70° C. (140-158° F.) by vaporizing the isobutylene into a rapidly stirred solution of 5 per cent by weight of concentrated sulfuric acid in p-cresol. The time of introducing the isobutylene can be varied from several hours to a few minutes and is limited only by the heat transfer surface available to carry away the heat of reaction. Polymerization of isobutylene to diisobutylene and triisobutylene always accompanies alkylation as a side reaction, and the amount of this polymer formed is partly dependent upon the time of reaction. Excessive time may yield 10-20 per cent of polymer by weight of the alkylate, whereas a reaction time of 10 minutes may give as little as 2-3 per cent of polymer with the production of better than 90 per cent of dibutyl p-cresol in the alkylate.

Although these observations are qualitative, they show that the rate of addition of isobutylene to phenols is high. When the isobutylene is in the vapor phase, as it should be for minimum polymer formation, the rate of absorption of the gas into the liquid cresol-catalyst phase is the controlling factor. When alkylations were run under sufficient pressure for the isobutylene to be added as a liquid, relatively large proportions of polymer were formed; this was probably because the degree of mixing at the point of contact was not sufficiently violent to prevent high instantaneous concentrations of isobutylene, leading to excessive polymer formation. At some future time the absolute reaction rates of isobutylene with phenols will be measured in a flowing system of proper design so that it will be unnecessary to consider mixing and diffusional effects.

A highly satisfactory type of batch alkylator was used in the early experiments; a 150-gallon V-bottom tank contains cooling coils, and to its bottom is connected the suction of a centrifugal pump discharging through a tubular heat exchanger back to the tank. The full charge of cresol and acid

is added to the tank, and the solution is circulated rapidly by the pump while isobutylene vapors are fed to the discharge of the pump ahead of the heat exchanger as rapidly as heat can be removed from the system. When the heat liberated by the reaction starts to drop, the reaction is nearly complete, and it is time to transfer the alkylate to another vessel for washing with hot dilute caustic soda solution agitated with steam. In practice the liquid isobutylene from the *tert*-butanol dehydration unit was fed to a vaporizer just ahead of the point of introduction to the alkylator without intermediate storage. Familiarity with the alkylator enabled the operator to shut down the alcohol dehydrator when the alkylation reaction was completed without wasting isobutylene.

Catalysts

The study of various acid catalysts and modifiers is included in the fundamental work mentioned earlier and is not part of the chemical engineering investigations. However, concentrated sulfuric acid is one of the best and most active of all catalysts; for this reason, together with its cheapness and ready availability in most refineries, the process studies were confined to this one catalyst with excellent results. In most of the pilot plant work, 96-98 per cent acid was dissolved in the cresol charged to the alkylator in amounts equal to 5
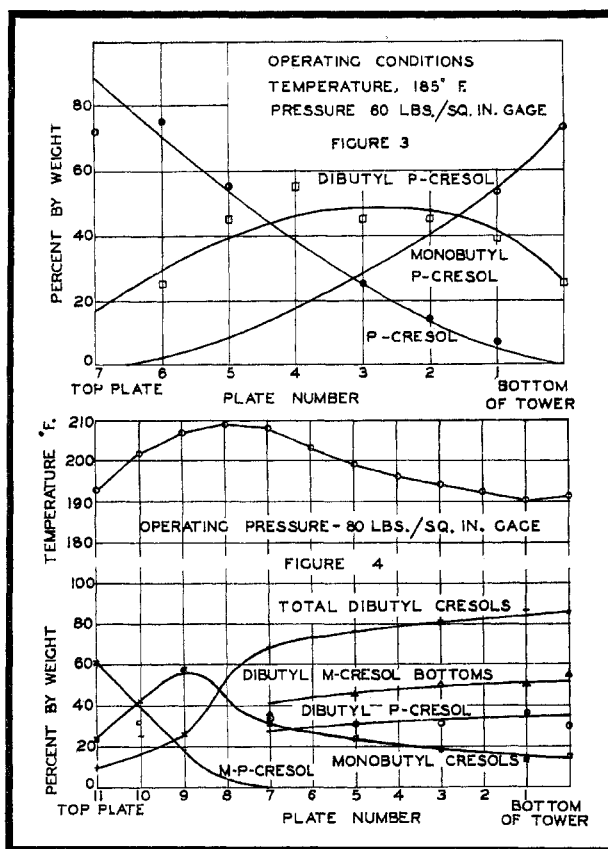

Figure 3. Plate-to-Plate Compositions for the Alkylation of p-Cresol in a 4-Inch Bubble-Cap Tower

Figure 4. Plate-to-Plate Compositions and Temperatures for the Semicommercial 16-Inch Bubble-Cap Reactor

Charge rate in cresol equivalent is 1038 pounds per day or 34.2 pounds per hour per square foot.

weight per cent of the cresol charge. In later commercial operations 104 per cent fuming acid was used, partly because of its availability and partly to compensate for small amounts of water dissolved in the monobutyl cresols returned to the system for realkylation along with the fresh cresol charge. Where recycle materials are present, the amount of acid catalyst to be added is calculated on the cresol equivalent of the mixture and not upon its total weight.

Only a narrow variation in catalyst concentration can be allowed without lessening the efficiency of the operation. Experiment has shown that less than about 3 per cent tends to lower the degree of alkylation, while much more than 5 per cent tends to produce excessive side reaction products such as isobutylene polymers and the formation of high-boiling residues. This is a phase of the work to which considerably more study could be devoted because the loss of cresols due to sulfonation and the formation of the butyl esters must be closely allied with the amount of acid used and its original concentration.

Continuous Studies

Early in this study it became evident that increasing quantities of alkylated cresols would be required. Process development was therefore directed toward the use of a refinery butane-butene fraction, derived from the thermal cracking of petroleum, as a source of isobutylene and a commercial cut of m-p-cresols as a source of the cresol isomers. As soon as equipment could be installed in a refinery, a combination of small-scale preparation and process development met the existing demands for the product. As demands increased, new equipment was gradually added to the pilot plant until it grew to semicommercial size. Continuous distillation equipment was installed for separating monobutyl cresols, dibutyl p-cresol, and dibutyl m-cresol.

The reaction of pure isobutylene and cresols is singularly clean-cut for no substance remains to contaminate the reaction product. However, when a refinery butane-butene fraction containing isobutylene is contacted with cresols, only the isobutylene reacts and the n-butenes and butanes remain as an additional phase of the reaction system. It is necessary, therefore, to devise a system whereby the isobutylene-containing gases are contacted with the cresol-acid phase and then are removed as rapidly as the isobutylene is absorbed.

These conditions are readily met by employing a packed tube as a contactor. The cresol-acid phase is fed as a liquid to the top, and the vaporous butane-butene stream enters at the bottom in countercurrent flow. The first reactor used in the laboratory was made of one-inch extra heavy tubing packed with $1/4$-inch stainless steel carding teeth and jacketed with water of the desired temperature for control. Series of continuous runs at four temperatures were made over a pressure range but at constant flow rates of gas and cresol-acid mix. Figure 1 shows the results when the butane-butene contained approximately 30 mole per cent isobutylene and about 25 mole per cent pentane-amylene hydrocarbons; the optimum pressure was 20 to 30 pounds per square inch gage. It is important that at the lower temperatures, the degree of alkylation drops off sharply with pressures in the range of 40 to 90 pounds. Raising the temperature from 55° to 75-83° C. largely nullifies the undesirable effects of the higher pressures. Since the capacity of an alkylator is almost a direct function of the operating pressure, it is desirable for the pressure to be as high as is consistent with good alkylation.

Understanding of the phase relations of catalyst, cresols, and butanes is important in interpreting the effects of temperature and pressure. Although concentrated sulfuric acid is miscible in all proportions with m-p-cresol, only a few per cent of dissolved butanes will precipitate the acid as a lower

phase. Further increases in butanes will eventually cause the separation of a third phase rich in butanes. The concentrated acid that separates them reacts with the olefins present in an alkylation system, and the result is the formation of polymers, sulfuric esters, and resinous materials and a consequent weakening of the catalyst activity. This is the chain of events that occurs in varying degree when the pressure in a mixed vapor- and liquid-phase alkylation system is too high or when the temperature is too low. The presence of hydrocarbons higher in molecular weight than butanes has the same effect as excessive pressure for they will dissolve preferentially in the cresol phase. For the same reasons isobutylene-propane mixtures can be employed at considerably higher pressures because of the reduced tendency for propane to liquefy.

The butane-butene used in the runs summarized in Figure 1 was abnormally high in both isobutylene and higher hydrocarbons. With a feed containing about 18 per cent isobutylene and 6 per cent pentane-amylene, other series of runs were made in which optimum alkylation was obtained at approximately 85 pounds for a temperature of 85° C. (185° F.). The increased pressure compensated for the reduced olefin content; and since a small proportion of higher hydrocarbons was present, the degree of alkylation was equal to that obtained previously at equivalent cresol charge rates. The change in composition of a typical butane-butene fraction is shown in Table I.

Table I.   Change in Composition of a Refinery Butane-Butene Fraction on Passage through the Alkylation Tower

	Butane-Butene, Molal %	
	Charged	Spent
Propane-propene	2.8	3.3
Isobutane	6.9	8.1
Isobutylene	18.2	3.8
n-Butenes	30.8	36.3
n-Butane	35.6	41.8
Pentane-amylene	5.7	6.7
	100.0	100.0

A few generalizations can be made on alkylation conditions:

1. The temperature of the reaction should be limited to approximately 100° C., particularly in that portion of an alkylation reactor where high concentrations of dibutyl cresols are present.
2. When sufficient vapor-liquid contact is provided—a condition that can be met in towers of nominal length—the capacity of a tower for any given set of operating conditions and yield is limited primarily by the allowable gas rate through the tower.
3. A large excess of isobutylene is advantageous only under conditions of poor alkylation. When conditions are correct, no advantage is to be gained from having more than 3-4 mole per cent isobutylene in the spent gas from the reactor, and for a charge gas containing 15-20 mole per cent isobutylene, this represents a recovery of 80-90 per cent.

Packed towers 6 and 10 inches in diameter were built and operated for a period, but neither was entirely satisfactory because of the horizontal temperature gradient that developed across the tower created by the heat of butylation of cresol. This value was estimated to be 640 B. t. u. per pound of isobutylene reacted with m-p-cresol.

Since it is unavoidable that packed towers develop horizontal temperature gradients, an experimental 4-inch bubble-cap tower was built and placed in continuous operation; it was fitted with

seven $2^5/_8$-inch bubble caps, each supported on a separate tray spaced about a foot apart. Each tray embodies an integral circular passageway through which water circulated, allowing individual temperature control. This unit was found to have a capacity almost equal to that of the 6-inch packed tower for p-cresol alkylation. A series of tests was made at a constant temperature of 185° F., at pressures varying from 30 to 90 pounds per square inch gage, and for flow rates from 13.6 to 54.4 pounds of p-cresol per hour per square foot of tower cross-sectional area. The data from these runs (Figure 2) show that at less than the optimum pressure of approximately 90 pounds per square inch, the flow rate markedly affects the degree of alkylation. For this pressure, however, the degree of alkylation is little affected by flow rates, and the capacity of the tower is determined by the amount of gas that will pass through without serious priming.

For a pressure of 60 pounds per square inch gage and a flow rate of 29.4 pounds of p-cresol per hour per square foot, samples of alkylate were withdrawn from each plate and analyzed. These analyses are plotted in Figure 3. p-Cresol first reacts with one mole of isobutylene to form monobutyl p-cresol. The concentration of the monobutyl derivative passes through a maximum of 50 per cent on about the middle tray of the bubble-cap tower and then drops off sharply at the bottom. The concentration of dibutyl p-cresol rises gradually to a concentration of about 75 per cent. Unfortunately for this example the operating pressure was 60 pounds per square inch. If 90 pounds had been used, the degree of dibutylation would have been increased to 90 per cent or better. The peak of the monobutyl curve for the reaction at higher pressure would have occurred nearer the top of the column, and its rise and fall would have been more abrupt.

This effect is shown in Figure 4 which represents a series of tests on one of the semicommercial alkylation columns of 16-inch diameter.

Analytical Methods

About 600 cc. of product are drawn into a quart bottle containing an excess of sodium carbonate solution for the neutralization of the acid catalyst. Sodium carbonate is preferable to sodium hydroxide because the carbonate does not dissolve cresols and monobutyl cresols. After shaking well and allowing small amounts of dissolved butanes to escape, approximately 350 cc. of the clear alkylate are weighed into the 500-cc. still pot of a $5/_8$-inch glass fractionating still, jacketed in the conventional manner for adiabatic operation and packed with $1/_8$-inch stainless steel carding teeth. A few grams of alcoholic potassium hydroxide solution are added to the still pot to neutralize soluble sulfuric esters as they decompose on heating. The still is operated first at atmospheric pressure to remove the light hydrocarbons, the diisobutylene, and the triisobutylene. When the vapor temperature reaches 185° C., or approximately halfway between the boiling point of triisobutylene and cresol, the still is cooled sufficiently for the distillation to be resumed under a vacuum of 20 mm. mercury absolute. Cuts of isobutylene polymers, monobutyl cresols, and dibutyl cresols are taken in weighed graduated cylinders, and the results of the assay are calculated on a weight basis. Light hydrocarbons such as butanes and pentanes are caught in the solid carbon dioxide–acetone bath.

Semicommercial Designs for Alkylators

Because of the marked success of the 4-inch bubble-cap alkylator over the larger and less efficient packed towers,
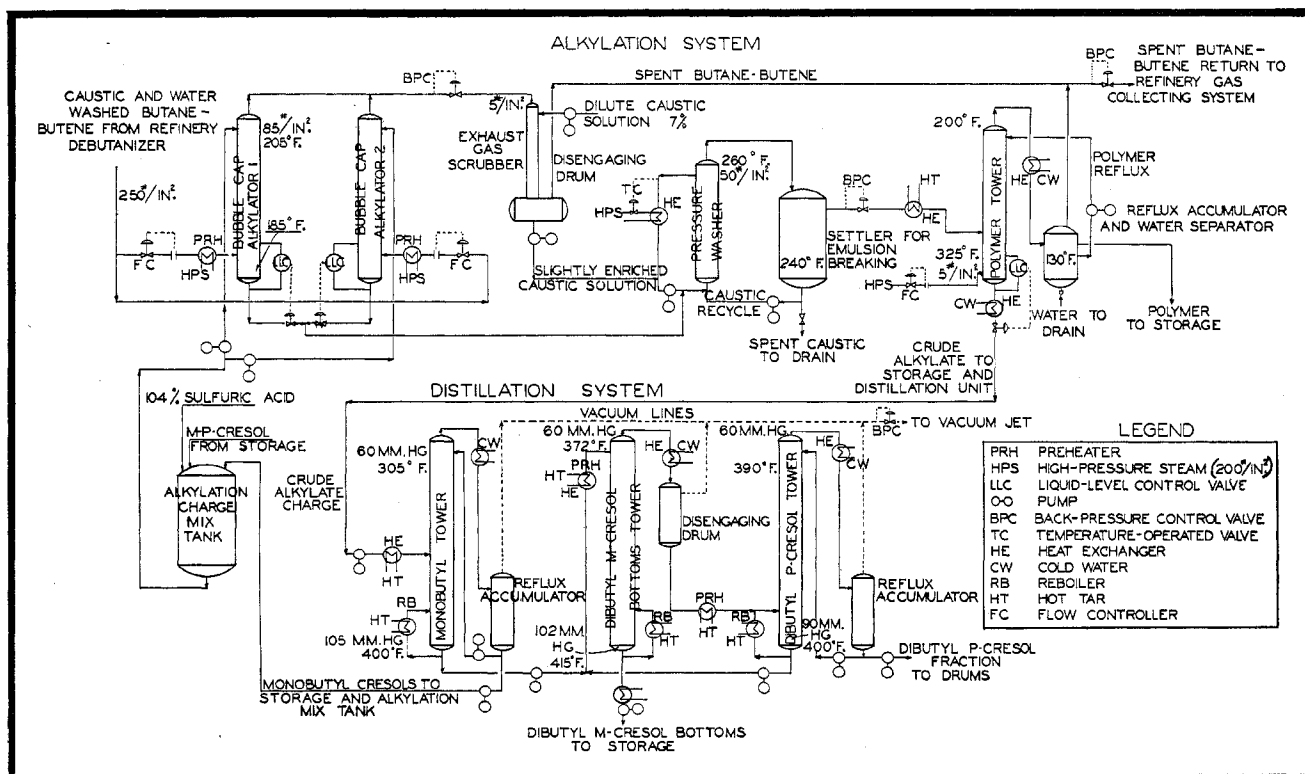

Figure 5.   *Alkylation and Distillation Systems of the Semicommercial Plant*

further emphasis was placed on the bubble-cap type of contactor. One problem, which is uncommon to ordinary fractionating tower design but is present here, is the transfer of the heat of alkylation from each tray. This has been accomplished by spacing the caps to allow cooling coils to be immersed in the liquid on the trays. Since pressure drop is unimportant, and the presence of the cooling coils necessitates a high liquid level to be carried on the trays, the bubble caps are deeply immersed for maximum vapor-liquid contact. For the eleven trays of the 16-inch tower, the spacing is 12 inches; each tray holds twelve pressed-steel bubble caps $2^3/_8$ inches in diameter. For the 20-inch tower, the tray spacing is reduced to $8^1/_2$ inches, allowing a tower of the same height to embody fifteen trays with twelve pressed-steel bubble caps of 3-inch diameter. Heat transfer surface for the 16-inch tower consists of helical coils of $^1/_2$-inch pipe of irregular shape spaced between the risers of the bubble caps. In the 20-inch tower, heat transfer surface consisted of three parallel lengths of straight tubing laid parallel to, but just clearing the trays between, the bubble-cap risers and welded through the walls of the tower. By connecting the tubes by flanged headers, ready access may be had for cleaning out scale or mud accumulating inside the tubes. A 6-inch flanged handhole is welded to the side of the tower between plates in order that the decks may be inspected and repaired. As yet no such adjustments have been found necessary and no detectable corrosion has taken place after several years of operation.
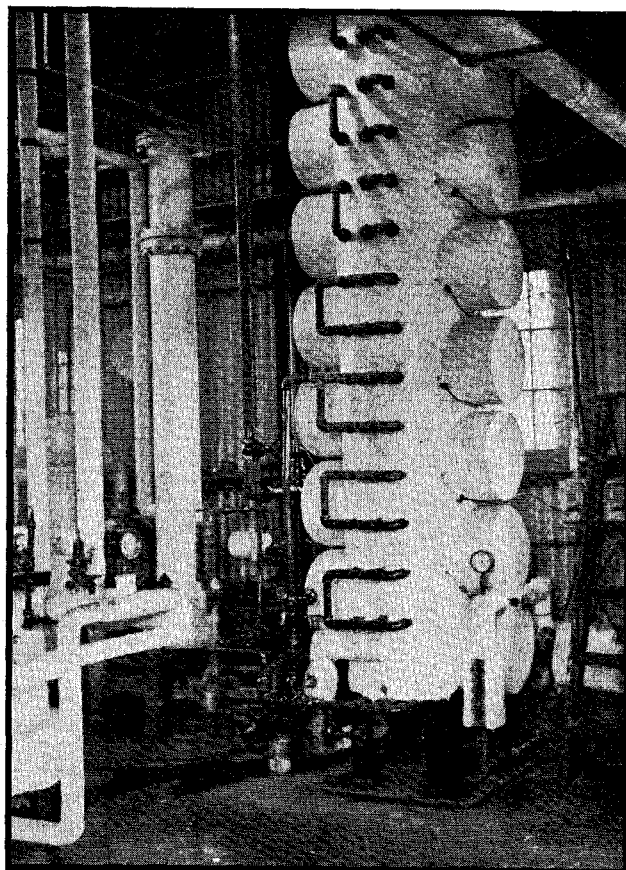
Alkylation

The semicommercial unit to be described comprises an alkylation system followed by a distillation system for the separation of a monobutyl m-p-cresol recycle stream for realkylation, a cut of dibutyl p-cresol, and a dibutyl m-cresol bottoms stream for subsequent handling.

The charge to the alkylators is made up in batches from the monobutyl recycle stream from the distillation towers, fresh m-p-cresol from storage, and 5 per cent by weight of 104 per cent fuming sulfuric acid, based on the cresol equivalent content of the mixture and not on the total weight of the charge. It is then picked up and pumped separately to the 16-inch and the 20-inch bubble-cap alkylators operated in parallel (Figure 5). After thorough caustic and water washing of the refinery butane-butene to remove sulfur compounds, the gases proceed through flow controllers to preheaters where vaporization and preheating to about 200° F. take place, to the bottom sections of the alkylators. The alkylated cresols accumulate in the bottom sections of the towers and continuously pass through liquid-level control valves to the pressure washing system.

Temperature control is maintained in the towers by circulating water at a high rate through the heat transfer tubes located on each tray. Circulation is from the top of the tower downward. Since both the heat transfer surface available and the amount of water circulating are large in comparison to the heat to be transferred, only a small temperature difference is required between the water circulating and the reaction product. This is particularly important to avoid overcooling the lower trays in the tower where the heat load is small compared to that in the top of the tower. Temperature control of the circulating water system is maintained by an automatic temperature valve which allows the correct proportion of cold water to enter the system to maintain a constant temperature.

The butane-butene passing through the towers gives up from 80 to 90 per cent of its isobutylene without any detectable change in the other constituents (Table I). Because of the elevated temperature at the top of a tower, the spent butane-butene picks up a small amount of cresol vapors

20-Inch Bubble-Cap Alkylation Tower in Semicommercial Unit

which are scrubbed by precontact with the caustic soda solution required to neutralize the acid alkylate. Any trace of sulfur dioxide produced by the reduction of the sulfuric acid catalyst is thus prevented from entering the refinery gas system.

Pressure Washing and Polymer Removal

The acid alkylate from the towers is injected through a stainless steel nozzle into the pressure-washer circulating system where an emulsion of alkylate and dilute caustic is maintained at about 260° F. and 50 pounds per square inch for neutralization of free acid and for the decomposition of potential acid-forming bodies. Circulation is several hundred times the throughput; the average residence time is thus about 40 minutes. A recycle from the bottom of the emulsion settler, into which the effluent from the washer goes, is maintained so that the emulsion shall contain not less than about 25 per cent of the aqueous phase. The fresh caustic solution alone amounts to only about 5 per cent by volume of the alkylate. Since an appreciable amount of butane and other light hydrocarbons is dissolved in the alkylate as it leaves the alkylators, the upper effluent from the settler is partly in vapor phase and includes steam from the washing operation. This mixture then passes through a preheater into the polymer
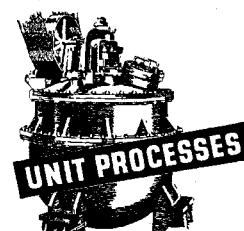
Table II. Physical Properties of Cresols, Xylenols, and tert-Butyl Derivatives

Compound	Melting Point, °C.	Specific Gravity (t/4° C.)				Boiling Point, °C.			Viscosity, Centistokes		
		Solid	80° C.	120° C.	160° C.	20 mm.	100 mm.	760 mm.	80° C.	120° C.	160° C.
o-Cresol	30.0	......	0.994	0.960	0.924	90	125.5	190.8	1.47	0.784	0.515
6-tert-Butyl-2-methylphenol	27	......	0.924	0.894	0.864	118	159	231	1.60	0.906	0.610
4-tert-Butyl-2-methylphenol	27	......	0.929	0.899	0.869	132	174	247	4.40	1.58	0.865
4,6-Di-tert-butyl-2-methyl-phenol	51	0.940 (26.7/4)	0.891	0.862	0.833	149.5	194	269	4.75	1.90	1.080
m-Cresol	11.5	......	0.986	0.954	0.921	101	138	202.2	1.76	0.890	0.570
x-tert-Butyl-3-methylphenol	21.3	......	0.922	0.892	0.862	129	171	244	2.12	1.03	0.642
4,6-Di-tert-butyl-3-methyl-phenol	62.1	......	0.912	0.882	0.853	167	211	282	9.90	2.87	1.420
p-Cresol	34.7	......	0.986	0.954	0.921	101	138	202.1	2.00	0.992	0.620
2-tert-Butyl-4-methylphenol	51.7	......	0.922	0.892	0.862	126.5	167	237	2.55	1.17	0.713
2,6-Di-tert-butyl-4-methyl-phenol	70.0	1.048 (20/4)	0.899	0.870	0.841	147	191	265	3.47	1.54	0.920
2,4-Xylenol	27.0	......	...	...	...	105	143	210	...	...	...
6-tert-Butyl-2,4-dimethyl-phenol	22.3	......	0.917	0.888	0.859	131	174	249	2.10	1.06	0.670
2,5-Xylenol	74.5	1.063 (20/4)	0.965	0.932	0.899	105	143	210	1.61	0.825	0.528
4-tert-Butyl-2,5-dimethyl-phenol	71.2	1.001 (26.7/4)	0.939	0.911	0.883	151	193.5	264	8.30	2.28	1.130
o-Ethylphenol	−18	......	1.037 (20/4)	...	...	101.5	138.5	207	...	...	...
x-tert-Butyl-2-ethylphenol	...	......	...	...	...	129	...	...	...	...	...
y-tert-Butyl-2-ethylphenol	...	......	...	...	...	141	...	...	...	...	...
4,6-Di-tert-butyl-2-ethyl-phenol	30	......	...	...	...	156.5	...	...	...	...	...
Diisobutylene	...	......	0.7195 (20/4)	...	...	...	43.3	101	...	...	...
Triisobutylene	...	......	0.7590 (20/4)	...	...	70	109	177	...	...	...

towers where almost all the diisobutylene and most of the triisobutylene, together with all butanes, pentanes, and steam are separated from the alkylate. These lighter constituents are usually in large enough proportions to strip out the triisobutylene, but in some cases superheated steam is added to the bottom of the tower as an additional stripping agent. The reflux accumulator serves also as a water separator.

Distillation

The crude alkylate, now essentially free from water and the light hydrocarbons, is pumped from storage to the continuous distillation system which is conventional except for necessary modifications caused by the equipment at hand (Figure 5). The three towers are each 10 inches in diameter and are packed with $1/_2$-inch Berl saddles which appear to give, under the conditions of vacuum operation employed here, H. E. T. P. values varying from 12 to 30 inches. The first tower serves to separate the monobutyl recycle containing about 10 per cent of dibutyl p-cresol. The dibutyl p-cresol fraction is separated from the dibutyl m-cresol bottoms in two towers instead of one in order to increase the separation without necessitating undue height of tower and pressure drop. Bottoms from the monobutyl tower along with bottoms from the dibutyl p-cresol tower are fed to the top of the second tower. Overhead from this tower is condensed, goes to a disengaging
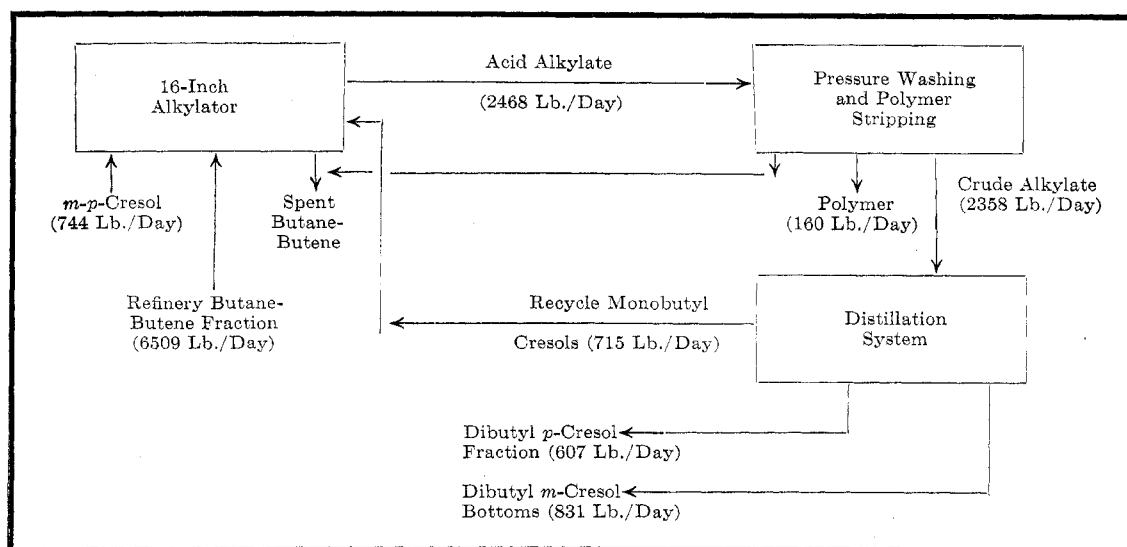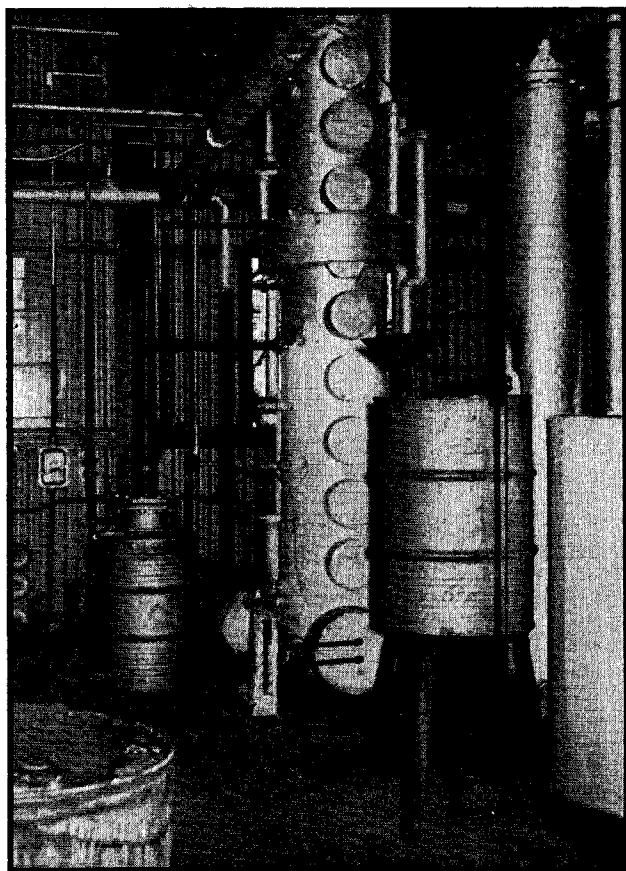

Figure 6. Plant Balance on Alkylation and Distillation Units Using 16-Inch Alkylator Only
(All Quantities Expressed as Pounds per Stream Day)

16-Inch Bubble-Cap Alkylation Tower Reactor

drum on which vacuum of 60 mm. mercury absolute is maintained, and proceeds from the bottom of this drum by gravity through a revaporizer to the bottom of the third tower. Dibutyl *p*-cresol product is taken from the top of the third tower, while the dibutyl *m*-cresol bottoms are withdrawn from the second tower. This gives the same results as though the third tower were added to the second tower and operated as a single unit.

Sufficient reboiler capacity has been provided to allow operation at reflux ratios of 3:1 to 5:1. Heat to reboilers and preheaters is given up by hot cracking still tar which flows from an external circulating system maintained at constant temperature and pressure by automatic valves. Circulation is accomplished in this system by a typical refinery hot oil pump, and the temperature is held in the range 500° to 550° F. by allowing just sufficient hot tar from the refinery at about 680° F. to enter the circulating system.

Problems of Semicommercial Operation

PRESSURE WASHING. It is absolutely essential that all potentially acid-forming material be removed from the crude alkylate in order that dealkylation will not occur in the distillation unit. The sulfur content should be reduced to less than 0.1 per cent by weight or to a point below which added contact time in the washer causes no further reduction. A contact time of at least 30 minutes is desirable at 260° F. The spent caustic should not be allowed to drop much below 2 per cent sodium hydroxide by weight for the best results, although it is believed that washing at higher pressures and

temperatures or at longer contact times might reduce the allowable minimum caustic concentration. The spent caustic leaves the unit saturated with cresol and monobutyl cresols which may be recovered by benzene extraction of the spent wash water. This loss amounts to about 1 per cent of the cresol equivalent charged. On the scale of operation carried out here, wash water recovery was not justified economically.

POLYMER TOWER. The primary reason for the installation of the polymer tower is to remove hydrocarbons that are largely vapors at 60 mm. mercury pressure because of their effect in reducing the capacity of the distillation system. Analysis of the polymer reveals that it contains mostly di- and triisobutylene, but it also contains small quantities of the butyl alcohols which appear in an analytical distillation as the diisobutylene azeotrope boiling at about 80° C. Diisobutylene boils at 102–103° C. The water separating in the polymer tower reflux accumulator contains about 5 per cent butanol-water azeotropes; the greater proportion is *tert*-butanol. However, a small but definite proportion of the azeotrope of *sec*-butanol is always found.

Purity of Distillation Products

The commercial *m-p*-cresol used (with 3° C. boiling range) contains from 3 to 5 per cent of other phenolic compounds as impurities. These compounds and their alkylated derivatives are listed in Table II. *o*-Cresol, 2,4-xylenol, and 2,5-xylenol were identified either through their alkylated derivatives or by dealkylation of certain fractions and identification of the parent compound. As Table II shows, the monobutyl derivatives of *o*-cresol and of *o*-ethylphenol boil in about the same range as the corresponding *m-p*-cresol compounds. This means simply that a certain small concentration of monobutyl impurities will circulate. The monobutyl derivative of 2,4-xylenol boils slightly above the other monobutyls and, therefore, comes out gradually with the dibutyl *p*-cresol fraction. The monobutyl derivative of 2,5-xylenol and the dibutyl derivatives of both *o*-cresol and *o*-ethylphenol boil at essentially the same point as does dibutyl *p*-cresol. Dibutyl *m*-cresol is unique in its boiling point which is 10° C. higher than that of any of the known impurities. These observations are well borne out in practice for a dibutyl *m*-cresol bottoms containing essentially no lower boiling material will dealkylate to 98–99 per cent *m*-cresol; whereas even a close-boiling dibutyl *p*-cresol fraction will yield on dealkylation only about a 92–95 per cent pure *p*-cresol. Thus the impurities are found to concentrate with the dibutyl *p*-cresol fraction; fortunately these impurities act only as diluents and have no adverse effect on the desired uses for the dibutyl *p*-cresol fraction. It is possible, however, to eliminate all these impurities by extremely sharp prefractionation of the *m-p*-cresol charge.

Material Balance on Plant Operation

The catalytic addition of tertiary butyl groups to phenols is a markedly efficient process when considered in the light of many organic syntheses. The reactions are singularly clean-cut and are little beset with extraneous products. The loss of isobutylene to the polymers di- and triisobutylene is of small consequence because such polymers may be used directly in motor fuel, they may be depolymerized to produce more isobutylene, they may be used directly to alkylate phenols if there is demand for the tertiary octyl derivatives, or the diisobutylene may be hydrogenated to isooctane. In the following paragraphs a balance has been struck on the operation show-
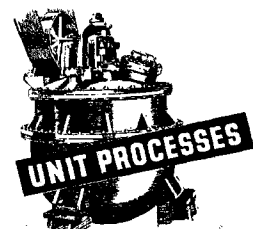
Table III. Composition of Streams in and from the Semi-commercial Unit

	Crude Alkylate, Charge to Distn. Unit	Mono-butyl Cresol Recycle	Polymer	Dibutyl Para Cresol Fraction	Dibutyl m-Cresol Bottoms
Butanes, pentanes, etc.	...	...	8.5	...	...
Diisobutylene azeotropes with butanols	...	...	10.5	...	...
Diisobutylene / Triisobutylene	6.2	13.5	{46.0 / 30.5}	...	...
m-p-Cresol	...	4.5	...	...	...
Monobutyl cresols	23.8	72.0	4.5	7.0	...
Dibutyl p-cresol	28.1	10.0	...	92.0	...
Dibutyl m-cresol	37.9	...	...	1.0	90.5
Residue[a]	4.0	...	...	...	9.5
	100.0	100.0	100.0	100.0	100.0

[a] Consists of about half alkylated phenol-type compounds boiling above dibutyl m-cresol and half nonvolatile compounds of a resinous or tarry nature; this residue also contains essentially all the sulfur in the alkylate.

ing the compositions and amounts of the streams in the plant with the attendant losses.

Table III lists the analyses of the various streams in the plant, and Figure 6 shows the relative quantities of each stream. After being stripped, the first of these streams (the crude alkylate) contains 6.2 per cent isobutylene polymers, of which the majority is triisobutylene. Monobutyl cresols average 23.8 per cent, with 28.1 per cent dibutyl p-cresol, 37.9 per cent dibutyl m-cresol, and 4.0 per cent high-boiling residue. This residue consists of about 50 per cent alkylated cresol-type compounds boiling higher than dibutyl m-cresol and about 50 per cent nonvolatile resinous or tarry matter formed as a by-product in the alkylation. Included in this portion are essentially all products containing sulfur. The monobutyl cresol recycle stream contains, in addition to 72.0 per cent monobutyl cresols, 13.5 per cent isobutylene polymers, 4.5 per cent unreacted m-p-cresol, and approximately 10 per cent dibutyl p-cresol. The stream designated as polymer is an overhead stream from the alkylate before it is fed to the fractionating columns and contains a variety of products. The first product to distill in an analysis of this stream is a fraction of light hydrocarbons, consisting mainly of butanes and pentanes, followed by about 10 per cent of the butanol azeotropes with diisobutylene. The remainder is isobutylene polymers and a small proportion of partially alkylated cresols. As mentioned previously, the dibutyl p-cresol fraction is the stream in which most of the impurities concentrate; 7.0 per cent of this fraction is listed as monobutyl cresols, but this portion also contained the alkylates from certain of the xylenols. Only about 1.0 per cent of higher boiling compounds are pres-

ent in this fraction, leaving the remainder of 92.0 per cent as dibutyl p-cresol. The dibutyl m-cresol bottoms contain essentially no lower boiling compounds but here is concentrated all of the residue formed in the crude alkylate charge.

To visualize the interrelations of the stream to and from the various units, Figure 6 shows the use of the 16-inch alkylator only. Since the completion of the test run from which these data were taken, the capacity of the plant has been more than doubled by the addition of a second alkylator, 20 inches in diameter, whose capacity is about 1.5 times that of the 16-inch alkylator. In summarizing Figure 6, it might be pointed out that the yields of the dibutyl p-cresol fraction and of the dibutyl m-cresol bottoms are 80 and 110 per cent, respectively, making a total of 190 per cent as compared to a theoretical yield of 204 per cent for dibutylation. If it is assumed that the 9.5 per cent of residue in the dibutyl m-cresol bottoms contains no recoverable cresol equivalent and this assumption is borne out in practice, the total remaining dibutyl cresols (Figure 6) account for 91.3 per cent of the m-p-cresol charged. About a third of the 8.7 per cent loss can be charged to the cresols and partially alkylated cresols lost in solution in the wash water discarded from the pressure washing system. A second third can be attributed to handling loss which is inevitable in relatively small-scale operation of this type, and the remaining third can be charged against the residue.

Acknowledgment

The writer wishes to acknowledge the contributions of many members of these laboratories who participated in this project, and to mention particularly the work of E. J. Loew and J. B. Kirkpatrick who acted as foremen of the semicommercial plant, and of L. H. Huth who conducted the test run from which the majority of the data presented here were taken. This work could never have reached its present state of development without the unfailing cooperation of W. M. Crockett, superintendent of the Philadelphia Refinery of the Gulf Oil Corporation, and of his staff in the erection and operation of the plant.

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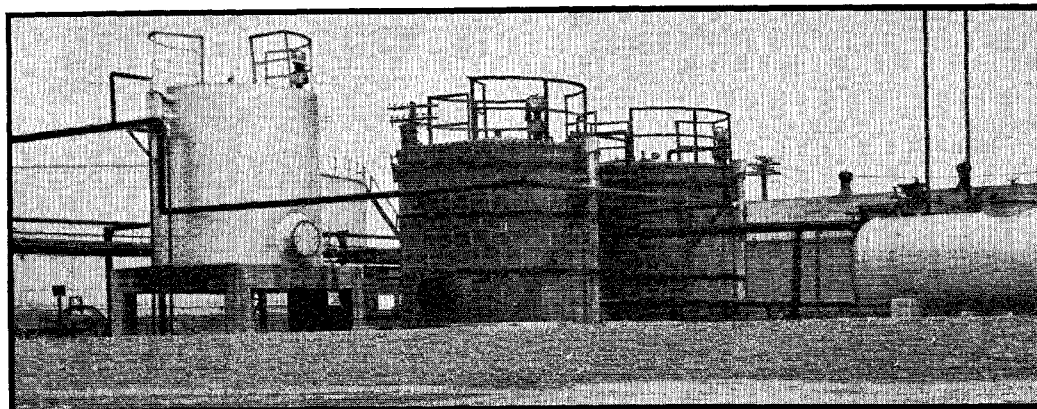
Storage Tanks for Alkylated Cresol Streams in the Semi-commercial Unit