Jan. 10, 1956 N. MAX ET AL 2,730,557

PRODUCTION OF ALKYL AROMATIC HYDROCARBONS

Filed March 2, 1954 2 Sheets-Sheet 1

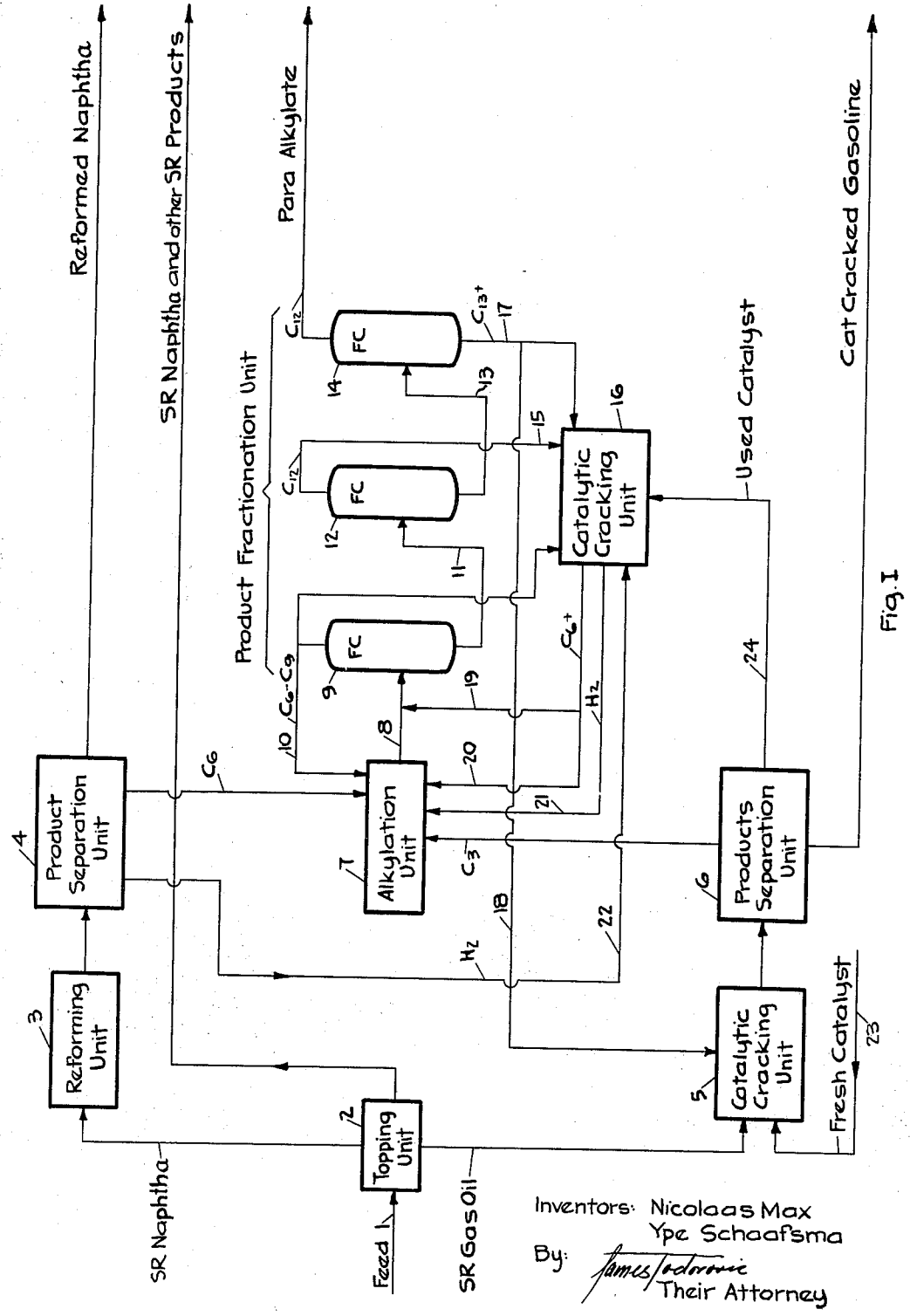


Fig. 1

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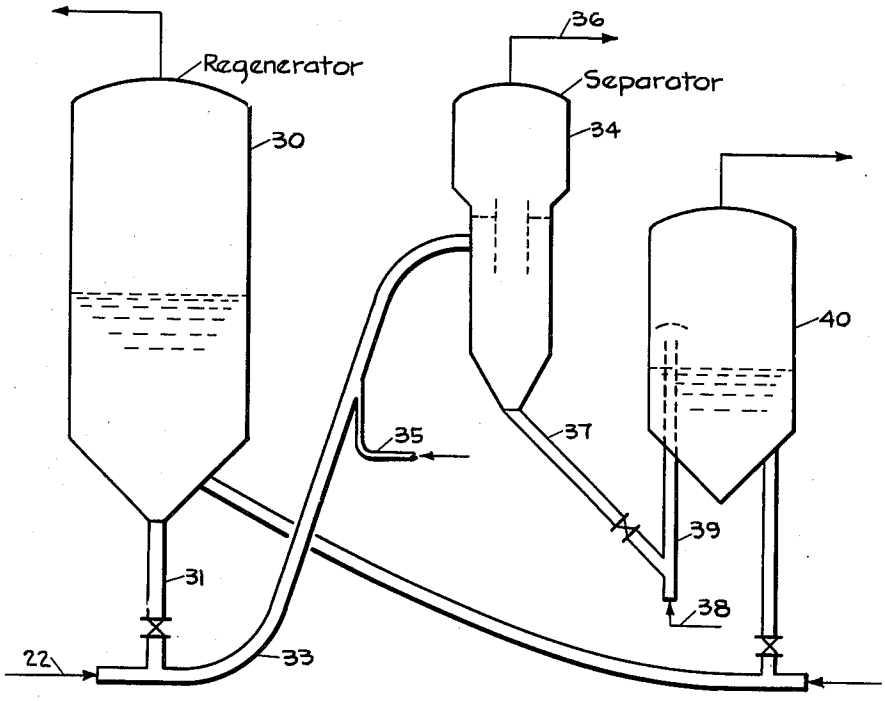


Fig. II

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PRODUCTION OF ALKYL AROMATIC HYDROCARBONS

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Claims priority, application Great Britain March 6, 1953

2 Claims. (Cl. 260—671)

This invention relates to the conversion of hydrocarbons primarily to dialkyl benzenes. More particularly the invention relates to a combination of process steps by means of which paradialkyl benzenes and especially para-diisopropyl benzene may be produced in good yields with a minimum loss to products of low value.

In the refining of petroleum, and more specifically the various cracking and reforming operations involved in such refining, considerable amounts of propylene are formed. It has been the practice to polymerize this propylene, either by itself or in conjunction with butylene, to produce liquid polymer products which may be blended with the gasoline either as is or after hydrogenation. In the alternative, the propylene may be used to alkylate aromatic hydrocarbons such as benzene, toluene, xylene, and the like, and the alkylate can be incorporated in the gasoline or other fuel as a blending component. However, such alkylate consists of the various isomers which differ widely in suitability and as a consequence the mixture has only a nominal value as a blending component. Thus, for example, the para-isomers are generally excellent components having very high blending octane numbers and rich mixture ratings whereas the meta- and ortho-isomers are comparatively poor components. Also, the para-isomers find wider application in other fields such as for instance, in the chemical field.

It is found that the desired para-dialkyl benzene may be produced to the substantial exclusion of other products by the following described process, the essential feature of which is in choosing the reactants and conditions and combining the steps in such a manner that continuous operation can be effected without excessive build-up of side reaction products and consequent requirement of a large bleed stream. In the first place, in order for the process to be economical, it is necessary that the desired product be separable from the gross product by ordinary fractional distillation. This can be readily accomplished in the case of the isomers of the poly-substituted isopropyl benzenes provided that interfering products are substantially excluded whereas it is not possible with the methyl and ethyl homologues. Secondly, although it is possible to react propylene with toluene, ethyl benzene, butyl benzene, xylenes, etc., the products generally boil outside of the gasoline boiling range. It is therefore preferred to utilize benzene or a benzene-rich fraction in the process.

The process of the invention in broad outline comprises the steps of alkylating benzene with propylene to produce a mixture of alkylated benzenes containing substantial amounts of the isomeric diisopropyl benzenes, fractionating the product to separate a fraction of diisopropyl benzenes and a fraction of heavier alkylated products including tri- and tetra-isopropyl benzenes, fractionating the isopropyl benzenes to separate a fraction containing most of the ortho- and meta-isomers, and a fraction containing the para-isomer, cracking the fraction containing the ortho- and meta-isomers and also, if desired, part of the heavier products under special conditions to produce primarily the mono-isopropyl benzene with a minimum of hydrogen

transfer reaction whereby the buildup of secondary reaction products in the system is minimized, recycling unconverted products in the cracking step, cycling the converted products to the alkylation step, and controlling the build-up of interfering products by a minimum bleed stream from the system.

The process will be described in more detail in connection with the description of a typical operation in which description reference may be had to the flow diagram in Figure I of the accompanying drawing.

The reforming and main catalytic cracking system shown in the flow diagram by blocks 3 and 5 are not essential to the process but are shown to illustrate how the process may be advantageously tied in with refinery operations.

Referring to the drawing, crude petroleum entering by line 1 is fractionated in a conventional topping section 2 into various straight-run products including a straight-run naphtha and a straight-run gas oil fraction. The straight-run naphtha is reformed in the reforming section 3, e. g., by the conventional platforming process, to produce a product rich in benzene and a gas consisting largely of hydrogen. These are separately recovered in the recovery section 4. The gas oil is catalytically cracked in the conventional manner in the catalytic cracking section 5 to produce the usual products, including propylene. The propylene is separated in the recovery section 6. The benzene and propylene are passed from the respective recovery systems to the alkylation section 7 and are converted therein to alkylate (a mixture of alkyl benzenes). Any of the conventional methods and alkylation catalysts may be used in this step. The alkylate is passed by line 8 to a fractionating column 9 wherein it is topped up to a temperature of about 198°–203° C. The overhead fraction containing unconverted benzene may be recycled to the alkylation unit by line 10. The bottom product from fractionating column 9 is passed by line 11 to a fractionating column 12 in which it is again topped to a temperature of about 204°–208° C. to produce an overhead fraction containing most of the ortho- and meta-diisopropyl benzene isomers. The bottom product from fractionating column 12 is passed by line 13 to a fractionating column 14 in which it is again topped to a temperature of about 209°–215° C. to produce as an overhead product a fraction of, or consisting largely of, para-diisopropyl benzene, and bottom fraction consisting largely of tri- and tetra-isopropyl benzenes.

The overhead product from fractionating column 12 is passed by line 15 to a second catalytic cracking section 16 operated under special conditions. If desired, all or part of the heavier fraction from line 17 may also be passed to this second catalytic cracking system or, if desired, this material may be returned in part or in whole by line 18 to the first catalytic cracking system 5. In the preferred operation this stream is split with part going to each catalytic cracking system for reasons which will be later explained. Also, in some cases, it may be desirable to pass the overhead fraction from fractionating column 9 to the catalytic cracking unit 16. This increases the load on the catalytic cracking system 16 but allows fractionating columns 9 and 12 to be combined into a single column.

If desired, the liquid product from the catalytic cracking system 16 may be recycled by line 20 to the alkylation unit 7. However, in order to decrease the volume of material passed to fractionating column 14, and also to recover small amounts of para-isopropyl benzene produced in the cracking step either by cracking of higher alkylated products or possibly by some small amount of isomerization, it is desirable to cycle this product by line 19 to the fractionating columns 9, 12, and 14. In the alternative this stream may be subjected to separate fractionation and only the benzene and mono-alkyl benzene

charged to the alkylation unit. The gaseous product from the catalytic cracking unit **16** is preferably cycled to the alkylation unit by line **21**. In the preferred embodiment the cracking in catalytic cracking unit **16** is carried out in the presence of a diluent such as steam or hydrogen which is advantageously the hydrogen gas produced in the reforming unit **4** and which is introduced by line **22**. The hydrogen in the effluent from the catalytic cracking unit may be advantageously separated in a system not shown and recycled in the catalytic cracking unit, or the separation may be effected in the alkylation unit itself in which case the alkylation is also carried out in the presence of added hydrogen.

In the system described the operation of the catalytic cracking unit **16** is critical. In normal catalytic cracking there take place, besides straight cracking, various other important reactions such, for example, as hydrogen transfer, polymerization, and condensation. Hydrogen transfer results in the conversion of unsaturated products to saturated products at the expense of hydrogen taken from material which is converted to the usual tars and so-called coke. This reaction is undesired in the present process since it leads to the build-up of saturated gases in addition to loss of valuable propylene. Polymerization and condensation do not normally occur to a large extent and are, therefore, relatively unimportant as far as the formation of higher boiling products are concerned. They are most important reactions, however, in regard to the present process since higher boiling products of these reactions are generally recracked to produce ethylene and especially large proportions of butylenes. These products, even when produced in only small overall percentages, are quite detrimental in the present process as they alkylate the aromatics in the alkylation step to produce mixed alkyl aromatics and higher boiling products which tend to build up in the system and make the necessary separation by fractional distillation impossible or at least impracticable. It is therefore necessary that the catalytic cracking in unit **16** be carried out in such a way, and under such conditions, that these reactions are minimized. This is preferably accomplished by employing low temperatures in the range of 300°–425° C. in the presence of at least 50% by volume of diluent gas and a selective catalyst. It may also be effected, although not as well, by operating at higher temperatures up to and including 500° C. provided that the conversion is severely limited by employing only very limited contact times of the order of 0.1 to 1 second. Under these conditions only a few per cent at most, e. g., 5% of benzene is found in the cracked products. Thus, for example, when operating at 350° C. with a contact time of 3.5 seconds only 1% benzene was found in the conversion products. At the same temperature but at a contact time of 11 seconds the concentration of benzene in the product was only 2.5%. On the other hand, when operating at 450° C. with a contact time of 3 seconds, the product contained 28% benzene and considerable side reaction products of the kind that interfere in the process. The actual contact time in seconds is difficult to determine accurately. However, it may be fairly estimated by calculating the volume of the total products per second at the reaction temperature and pressure, and dividing this quantity into the volume of the reaction space.

The catalytic cracking in unit **16** may be carried out with any of the conventional cracking catalysts; however, it is found that certain types of catalyst are better than others for the present purpose. Thus, Attapulgus clay and similar clays, supported phosphoric acid catalysts, and treated synthetic silica-alumina cracking catalysts (see below) are especially suited since they catalyze the mentioned undesired side reactions to a lesser degree and, therefore, allow operation with limited recirculation of ethyl and butyl alkylated products with lesser bleeding of the recycled stream. Ordinarily synthetic silica-alumina cracking catalyst, silica-magnesia cracking catalyst, and boric oxide-alumina cracking catalyst may be used but are inferior to those listed above.

The conventional silica-alumina cracking catalyst is rather unselective but may be made selective by treating it with steam. A suitable steam treatment reduces the available surface to around 350 m.²/g. or below. This treatment may be effected in a separate treatment. On the other hand, the catalyst receives an equivalent treatment during normal use in catalytic cracking. One can therefore use partially spent catalyst from the catalytic cracking unit **5**. Thus, fresh catalyst may be added to the catalytic cracking unit **5** by line **23** and partially spent catalyst from this unit may be passed by line **24** to the catalytic cracking unit **16** to supply the needs thereof. This arrangement results in advantages in both units.

In general, the catalytic cracking will be carried out using the catalyst in powdered form. However, other systems using fixed beds or moving beds of catalyst may be used. One suitable arrangement for obtaining the short contact time with powdered catalyst is illustrated in Figure II of the accompanying drawing. In this system the hot catalyst from a catalyst regenerator **30**, which may be a separate regenerator or the regenerator of a conventional unit in the catalytic cracking system **5**, is withdrawn by a standpipe **31** and is picked up and dispersed by a stream of gas diluent such as steam or preferably the hydrogen gas from line **22** (Figure I), and carried up through a tubular reactor **33** which discharges into a separation vessel **34**. The material to be cracked is injected by line **35** into the stream of hot dispersed catalyst at an intermediate point. After a short contact the vapors are immediately separated from the catalyst in the separator vessel **34**. The product vapors are withdrawn by line **36** while separated catalyst is withdrawn by line **37**. The spent catalyst is picked up and dispersed by steam entering via line **38** and carried by line **39** to a vessel **40** from which the catalyst is returned to the regenerator.

It will be apparent from the above that, while the alkylation step has been described with respect to the feeds produced, e. g., from the reforming unit **4** and catalytic cracking unit **5**, the alkylation actually is much more complicated since it involves alkylation of the quite different products from the catalytic cracking unit **16**.

As pointed out above, an important feature of the process described is in the means for minimizing the accumulation of side reaction products (which render difficult or impossible the desired separation of the product by commercial fractional distillation) to such an extent that the otherwise necessarily excessively large bleed stream (which would render the process essentially a once through process with low yields) may be avoided with consequent greatly increased yield and economy. While in the present process the required bleed stream is small, such a bleed stream cannot be dispensed with altogether. In the preferred embodiment of the process the bleed stream is withdrawn from line **17** by line **18**. The amount of material so withdrawn is preferably the minimum consistent with the ability to separate the desired product by commercial fractional distillation, e. g., in fractionating column **14**.

The overhead product from fractionating column **14** may be blended with the other usual refinery gasoline components in any desired proportion or combination to produce fuels of the desired characteristics or, if desired, part or all of this product may be directed to any other use for which it is suited.

Example

During a period of 5¼ hours a propylene fraction containing 318 kilograms of propylene was passed to an alkylation unit 7 containing 3590 kilograms of 88.2% sulfuric acid as catalyst and maintained at a temperature of 49°–52° C. The product from a catalytic cracking unit **16** consisting essentially of benzene and cumene was

likewise passed to the alkylation unit which resulted in the introduction of 4340 kilograms of cumene to the alkylation unit. The alkylation product (which contained 2085 kilograms of cumene, 1895 kilograms of diisopropyl benzene isomers, 388 kilograms of triisopropyl benzene, 94 kilograms of tetra-isopropyl benzenes, and 106 kilograms of heavy ends) was fractionated at atmospheric pressure whereupon 90% (665 kilograms) of the para-diisopropyl benzene was separated as product. The remaining ortho- and meta-diisopropyl benzene fraction (1230 kilograms) was passed to a catalytic cracking unit 16 wherein it was cracked at 500° C. with a catalyst consisting of alumina which had been treated with aqueous hydrofluoric acid solution to incorporate about 3% fluorine. At a space velocity of 1.7 kilograms per kilogram of catalyst per hour, the conversion was 75%, yielding a converted product containing about 84 mole % cumene and lesser amounts of benzene. The unconverted product was recycled to the catalytic cracking step and the converted product was passed to the alkylation step as described.

We claim as our invention:

1. Process for the conversion of hydrocarbons in part to para-dialkyl aromatic hydrocarbons which comprises in combination the steps of catalytically cracking alkylate obtained as hereinafter defined, separating from the products of said cracking a fraction consisting largely of cumene with minor amounts of benzene, passing the said fraction to an alkylation zone wherein it is alkylated with propylene, separating from the resulting alkylate by fractional distillation a fraction consisting largely of para-

diisopropyl benzene, passing to the said catalytic cracking a fraction consisting largely of ortho- and meta-diisopropyl benzene and catalytically cracking the same in the presence of at least 50% by volume diluent gas at a temperature between 300° C. and 425° C. under conditions whereby very little conversion to benzene, ethylene and butylenes is obtained, passing the cracked product to said alkylation zone as aforesaid, and retaining the concentration of alkyl aromatics having other than C_3 alkyl groups sufficiently low in the alkylation product to allow separation of said para-diisopropyl benzene by fractional distillation by withdrawing in addition to and separate from said para-diisopropyl benzene fraction a regulated portion of the alkylate boiling above said para-diisopropyl benzene fraction.

2. Process according to claim 1 further characterized in that the said catalytic cracking is effected with a cracking catalyst which has been steamed until its surface area is reduced to below 350 square meters per gram.

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