

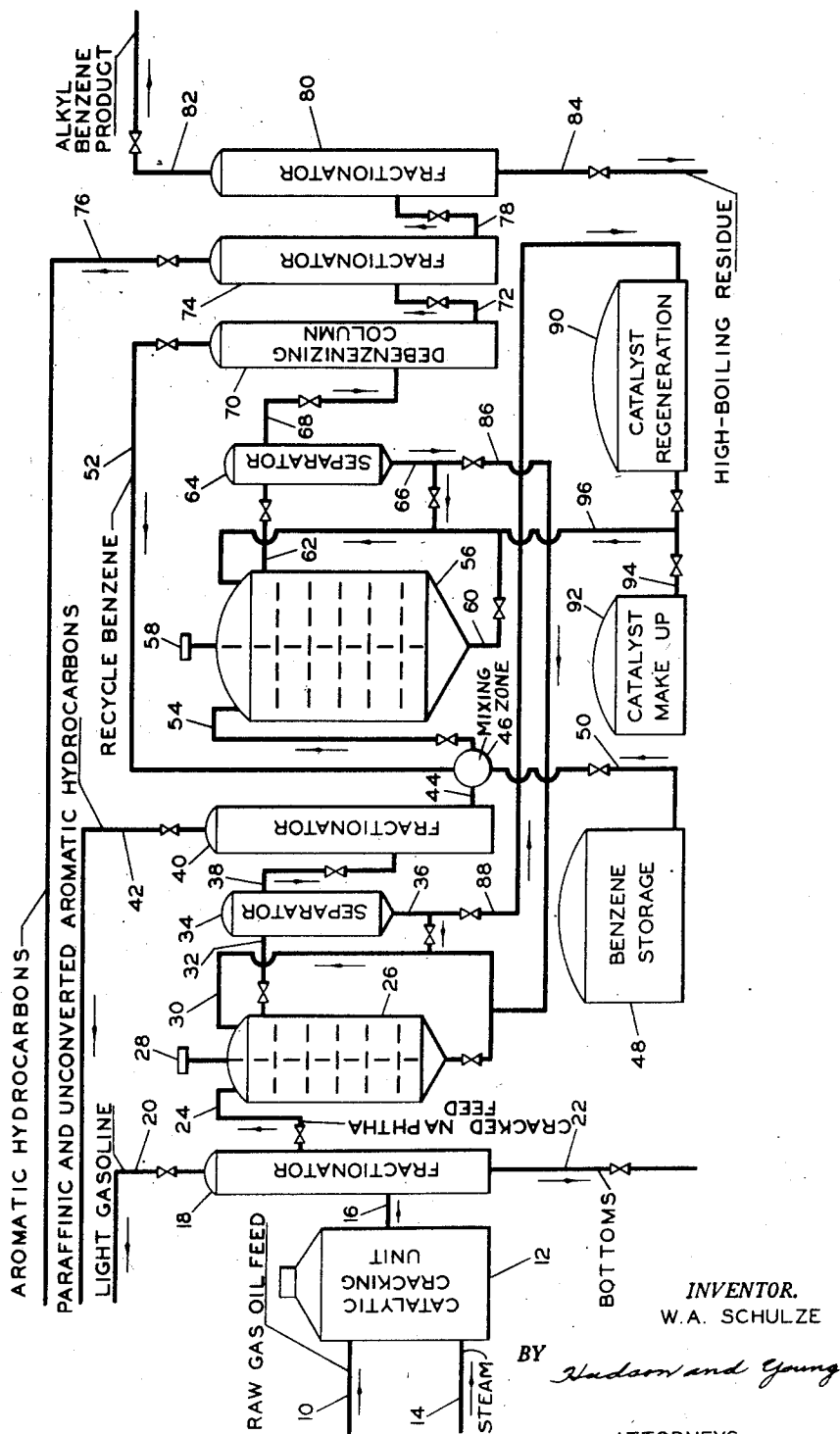
Dec. 12, 1950

W. A. SCHULZE

2,534,072

PRODUCTION OF ALKYL BENZENES

Filed June 2, 1947



UNITED STATES PATENT OFFICE

2,534,072

PRODUCTION OF ALKYL BENZENES

Walter A. Schulze, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

Application June 2, 1947, Serial No. 751,937

7 Claims. (Cl. 260—671)

1

This invention relates to the production of high molecular weight alkyl aromatic hydrocarbons. One embodiment of this invention relates to a two-step catalytic process for manufacturing alkyl benzenes. A specific embodiment of this invention relates to a continuous catalytic process wherein substituted and/or polynuclear aromatic constituents in a catalytically cracked naphtha fraction are alkylated with high molecular weight straight and branched chain olefins contained in the said fraction to produce high boiling alkylate mixtures which are subsequently admixed with a molar excess of benzene thereby effecting side chain transfer from the said high boiling alkylate mixture to the said benzene.

One prior method for the alkylation of aromatics with high molecular weight olefins discloses the use of an olefin concentrate comprising a fraction of a catalytically cracked naphtha containing substantial proportions of high molecular weight straight- and branched-chain olefins as the alkylating reactant for aromatic hydrocarbons in the production of alkyl benzenes. While numerous advantages are realized by operating in this manner, certain difficulties are inherent in the process. Cracked naphtha fractions of the type employed as alkylating reactants in the above mentioned method contain, in addition to the high molecular weight olefins, certain aromatic constituents comprising naphthalenes, alkyl and polyalkyl benzenes, and the like. The proportion of these aromatic constituents in the fraction is usually at least equal to and generally greater than that of the high molecular weight olefins contained therein. Therefore, when employing such a fraction as the alkylating reactant for, say, benzene in the production of alkyl benzenes, a competing reaction occurs wherein the residual aromatic constituents condense with the olefins present to produce undesirable high boiling alkylates. While the high boiling alkylates so formed may be separated in the fractionation of the product, their formation consumes a substantial amount of the olefins and proportionally diminishes the yield of desired product.

I have now discovered a process for the production of alkyl benzenes wherein the advantages realized from the use of the low cost olefin concentrates derived from catalytically cracked naphthas are retained and the difficulties hereinbefore mentioned are substantially reduced or entirely eliminated. The method of my invention comprises the following steps: (a) fractionating a catalytically cracked naphtha to pro-

2

duce a cut comprising olefins of at least seven and not more than eighteen carbon atoms to the molecule, in admixture with aromatic and paraffinic constituents boiling in the same range; (b) contacting said fraction with an alkylating catalyst under conditions for the condensation of the olefins present with aromatic constituents to produce high boiling alkylate mixtures; (c) separating and removing paraffinic and other hydrocarbons previously associated with the olefins; (d) admixing the alkylate with a molar excess of benzene and contacting with an alkylating catalyst under conditions for transfer of the high molecular weight alkyl group or groups added in the alkylation step from the high boiling alkylate to the benzene; (e) separating and removing unreacted benzene for recycle to the side chain transfer step; (f) separating and removing aromatic constituents recovered from the high boiling alkylate and discharging alkyl benzenes as product.

One object of this invention is to provide a process for the production of high molecular weight alkyl aromatic hydrocarbons.

Another object is to provide a two-step catalytic process for the manufacture of alkyl benzenes.

Another object is to provide a two-step continuous catalytic process for the production of alkyl benzenes whereby the aromatic hydrocarbons present in a cracked naphtha fraction are alkylated with olefins contained in the said naphtha fraction and the resulting high boiling alkylate mixed with a molar excess of benzene thereby effecting side chain transfer from the said high boiling alkylate to the said benzene.

Still another object of this invention is to provide a process for the production of alkyl benzenes suitable for use as detergent intermediates.

Other objects and advantages will become apparent to those skilled in the art from the accompanying discussion and description.

A significant feature of the present process lies in the utilization of the aromatic constituents of the feed stock as carriers for the olefins from the alkylation step to the side-chain transfer step. According to the precepts of my invention, alkylation of the aromatic nuclei proceeds to a high degree when the reaction time is short, polyalkylation often being the predominant reaction. Since the residual aromatic constituents in the feed stock comprise principally substituted nuclei, the resulting product from the alkylation step is a high boiling, largely polysubstituted alkylate mixture. On the other hand, with a longer

3

period of contact with an alkylation catalyst and in the presence of unalkylated nuclei, transfer of alkyl groups from the polyalkylate to the unalkylated nuclei takes place, those groups containing the larger number of carbon atoms being principally affected.

Thus by contacting the aromatic-olefin mixture comprised in the feed stock with an alkylating catalyst for a short time, generally between five and 40 minutes and preferably between 10 and 15 minutes, condensation of olefins with the residual aromatic constituents occurs to produce a high boiling alkylate in which the aromatic nuclei are substituted by one or more straight or branched chain alkyl groups in addition to substituent alkyl groups containing a less number of carbon atoms previously present. This high boiling product in admixture with a molar excess of benzene is contacted with an alkylating catalyst for a longer period of time, generally from 20 to 60 minutes, but preferably from 25 to 45 minutes. Under suitable conditions, side-chain transfer from the polysubstituted molecules of the high boiling alkylate to the unalkylated nuclei of the benzene is effected.

By operating in this manner, the losses incurred from formation of undesirable high boiling alkylates which were noted in previous operations employing highly olefinic naphtha fractions as alkylating agents are eliminated or substantially reduced. At the same time olefins of the feed stock are utilized to a high degree in the production of desirable alkylates, thus providing economic advantages of a major order.

Further advantages of the present invention will be apparent from an explanation of the accompanying drawing in which is shown a diagrammatic illustration for one specific embodiment of my process. While the drawing and explanation relates to the use of liquid type catalysts such as boron fluoride compositions, this particular embodiment is selected merely for simplicity in explanation, and is not limiting to the scope of the disclosure. Referring to the drawing, a charging stock comprising a high boiling naphtha or gas oil is introduced through line 10 into a catalytic cracking process 12 which may preferably be of a "Cycloversion" type in which, after preheating, the feed stock is combined with high temperature steam diluent introduced through line 14 and passed over a fixed bed bauxite type catalyst maintained at a temperature in the range of 900° F. to 1200° F. See article by Schulze et al., Oil and Gas Journal, April 13, 1944. In this type of unit the high boiling charging stock is catalytically cracked under non-polymerizing conditions to form a cracked naphtha characterized by its high content of unusually stable olefins having from 7 to 18 carbon atoms per molecule, and of aromatic and paraffin hydrocarbons. In the interest of simplicity in the drawing, catalyst chambers, fractionating and stabilizing columns, and the like which are elements of the cracking process are not shown in detail, their design and arrangement being conventional in nature.

The product from this unit is discharged through line 16 to fractionator 18 where light gasolines are removed overhead through line 20 for storage or utilization elsewhere. High boiling bottoms are discharged through line 22. A fraction distilling between about 200 and about 500° F. and comprising straight- and branched-chain olefins averaging at least seven and not more than eighteen carbon atoms to the molecule

4

in admixture with aromatic and paraffinic hydrocarbons is conveyed through line 24 to alkylation zone 26 where it is contacted with an alkylating catalyst which may suitably be a liquid complex or composition of boron fluoride under conditions such that the aromatic constituents are condensed with the high molecular weight olefins present. Other catalytically or thermally cracked naphthas may be used to prepare the desired charge to said alkylation zone. When operating with liquid type catalysts more effective contact is obtained by suitable agitation of the system by a mechanical stirrer 28. Also, since catalysts of this type are high density materials, it is desirable that a recycling catalyst circulation be provided from the bottom of the reactor through line 30.

From alkylation zone 26 the effluent is directed through line 32 to catalyst separator 34 where it is separated by gravity into catalyst and hydrocarbon phases. The heavier catalyst phase is removed through line 36 and restored to the circulating catalyst stream in line 38 while the hydrocarbon phase is discharged through line 38 to fractionator 40. Here paraffinic hydrocarbons and unconverted aromatic constituents are removed overhead via line 42 for storage or utilization elsewhere. This overhead fraction often has an aromaticity of sufficient magnitude to qualify it as an effective solvent naphtha.

The higher boiling residue comprising principally polysubstituted alkyl benzenes is conveyed through line 44 to mixing zone 46 where it is combined with a molar excess of benzene drawn from storage 48 through line 50 and from recycle line 52. The mixture is conveyed through line 54 to the side-chain transfer zone 56 where it is contacted with an alkylating catalyst which, in this specific embodiment, comprises a liquid type catalyst such as was employed in the alkylation zone 26. The volume of the reactor used for the side-chain transfer step of the process is larger than the alkylation reactor by a sufficient amount that with a flow rate which provides a contact time of 10 to 15 minutes in the alkylation zone, a contact time of 30 to 45 minutes is obtained in the side-chain transfer zone. Effective contact with the catalyst is obtained by agitation with mechanical stirrer 58 and by circulation of the catalyst through line 60. Conditions in the side-chain transfer zone are regulated in a manner such that transfer of straight and branched chain alkyl groups added in the alkylation zone from the polyalkylate to the benzene is effected.

From the side-chain transfer zone the effluent is conveyed through line 62 to separator 64 from which the heavier catalyst phase is removed through line 66 to be restored to the circulating catalyst stream in line 68. The hydrocarbon phase is passed through line 68 to the debenzenizing column 70 where unreacted benzene is removed overhead via line 72 for recycling to the side-chain transfer zone through mixing system 46. The debenzenized stream is then passed through line 72 to fractionator 74 where the aromatic hydrocarbons from which the high molecular weight straight- and branched-chain alkyl groups were removed in the side-chain transfer zone are separated and discharged through line 76 for storage or utilization elsewhere. The aromaticity of this lower boiling fraction is very high, often being as much as from 80 to 90 per cent, thus providing a valuable source for very high solvent power solvent naphthas. Crude alkyl benzenes are discharged via line 78 to fractionator

80 which may preferably be operated under reduced pressure. The alkyl benzene product is removed through line 82 and high boiling residues discharged via line 84. In some instances these high boiling products, which comprise largely polyalkyl benzenes, may be recycled to the side-chain transfer zone through line not shown for further treatment.

Alkylation of the residual aromatic compounds in the feed stock with the high molecular weight olefins contained therein is accomplished readily and can be effected in the presence of a catalyst of lower activity than that employed in the side-chain transfer step. A preferred method of operation therefore is to convey catalyst previously employed in the side-chain transfer step from line 66 via line 86 for introducing into line 30 as catalyst feed to the alkylation zone 26. When operating in this manner, spent catalyst is removed from the alkylation zone via line 88 and conveyed to regeneration zone 90. Regenerated catalyst together with such make-up as needed, the said make-up being drawn from storage 92 via line 94, is introduced into the side-chain transfer catalyst system via line 96.

In the accompanying diagrammatic drawing reference to some of the equipment such as pumps, gauges, and other equipment which obviously would be necessary to actually operate the process have been intentionally omitted. Only sufficient equipment has been shown to illustrate the process of the invention and it is intended that no undue limitation be read into this invention by reference to the drawing and discussion thereof.

The catalyst to be employed in the alkylation and side-chain transfer zones of my process is a liquid type such as anhydrous hydrogen fluoride; boron fluoride complexes or compositions, which complexes or compositions may comprise boron fluoride and water, boron fluoride and phosphoric acid, boron fluoride and hydrogen fluoride or boron fluoride and aqueous hydrogen fluoride. Highly effective results can also be obtained by the use of hydrofluoric acid as the catalyst in aqueous solutions of 50 per cent or higher concentration.

Temperatures in the reaction zones will generally be in a range between 60 and 140° F., and preferably between 80 and 125° F. The reactions can be effected without the use of superatmospheric pressures but it is usually preferable to apply sufficient pressure to avoid vaporization of the catalyst; for example, pressure of from 30 to 50 pounds per square inch gauge is sufficient. The volume ratio of benzene to alkylate in the side-chain transfer step will be between 2:1 and 15:1, preferably from 5:1 to 10:1. The volume ratio of catalyst to hydrocarbons in both the alkylation zone and the side-chain transfer zone will vary considerably depending upon the particular catalyst and other variable factors, but usually a ratio in the range of 1:1 to 1:5 in each zone is satisfactory.

The foregoing disclosure relates particularly to the alkylation of benzene with olefins from an olefin concentrate. However, the process is applicable to the alkylation of aromatic hydrocarbons containing a substituent alkyl group such as toluene. Polysubstituted benzenes such as the xylenes may be employed in some instances although side-chain transfer is less readily effected as the number of substituent alkyl groups approaches that which exists in the polyalkylate from the alkylation step.

Example

A high-boiling naphtha was subjected to catalytic cracking by a "Cycloversion" process. The product was fractionated to yield a cut boiling in the range 400 to 450° F. and comprising about 20 per cent high molecular weight olefins. A sample of the naphtha so prepared weighing 1,652 grams was contacted with a catalyst consisting of 50 per cent aqueous hydrofluoric acid saturated with boron fluoride gas for a period of 20 minutes at a temperature of 120-130° F. Fractionation of the effluent yielded 435.7 grams of alkylate boiling above 690° F. This product was commingled with 765 grams of benzene and contacted with the catalyst for a period of one hour, conditions being maintained as before. Fractionation of the effluent yielded 310 grams of alkylate boiling in the range 550 to 680° F.

It is to be understood that this invention should not be unnecessarily limited to the above discussion and description and that modifications and variations may be made without departing substantially from the invention or from the scope of the claims.

I claim:

1. A two-step process for catalytically producing high molecular weight alkyl benzenes, which comprises fractionating a catalytically cracked naphtha to produce a fraction containing olefins having at least seven and not more than eighteen carbon atoms to the molecule and alkylatable aromatic constituents; contacting said fraction with a liquid type alkylation catalyst in an alkylation zone under conditions such that said olefins react with said aromatics; separating effluent reaction mixture from said alkylation zone into a catalyst phase and a hydrocarbon phase in a separation zone; introducing said hydrocarbon phase into a fractionation zone, removing unreacted hydrocarbons previously associated with the olefin-aromatic containing fraction; mixing the resulting high-boiling alkylate with excess benzene in a mixing zone, contacting resulting mixture in a side-chain transfer zone with a liquid type alkylation catalyst under conditions to effect side-chain transfer from said high-boiling alkylate material to unalkylated benzene; separating effluent reaction mixture from said side-chain transfer zone in a separating zone into a catalyst phase and a hydrocarbon phase and recovering high molecular weight monoalkyl benzenes from said hydrocarbon phase.

2. A two-step process for catalytically producing high molecular weight alkyl benzenes, which comprises fractionating a catalytically cracked naphtha to produce a fraction containing olefins having at least seven and not more than eighteen carbon atoms to the molecule and alkylatable aromatic constituents; contacting said fraction with a liquid type alkylation catalyst in an alkylation zone under conditions such that said olefins react with said aromatics; separating effluent reaction mixture from said alkylation zone into a catalyst phase and a hydrocarbon phase in a separation zone; introducing said hydrocarbon phase into a fractionation zone; removing unreacted hydrocarbons previously associated with the olefin-aromatic containing fraction; mixing resulting high-boiling alkylate material with excess benzene in a mixing zone, contacting resulting mixture in a side-chain transfer zone with a liquid type alkylation catalyst under conditions to effect side-chain transfer from said high-boiling alkylate material to un-

alkylated benzene; separating effluent reaction mixture from said side-chain transfer zone in a separating zone into a catalyst phase and a hydrocarbon phase; recycling at least a portion of said catalyst phase to said alkylation zone; introducing said hydrocarbon phase into a debenzenizing zone and removing unreacted benzene from said hydrocarbon phase; introducing remaining hydrocarbon phase into a fractionation zone, removing low-boiling aromatic constituents resulting from the side-chain transfer reaction in said transfer zone, introducing resulting alkyl benzene material into a second fractionation zone and removing monoalkyl benzenes as a product of the process.

3. A two-step process for catalytically producing high molecular weight alkyl benzenes, which comprises fractionating a cracked naphtha to produce a fraction containing olefins having at least seven and not more than eighteen carbon atoms to the molecule and alkylatable aromatic constituents; contacting said fraction with liquid type alkylation catalyst in an alkylation zone; maintaining temperature in said alkylation zone in a range of 60 to 140° F.; maintaining pressure in said alkylation zone sufficient to prevent vaporization of said catalyst; maintaining a volume ratio of catalyst to said fraction in alkylation zone in the range of 1:1 to 1:5; maintaining rate of flow of said fraction and catalyst such that the residence time in said alkylation zone is in the range of 5 to 40 minutes; separating effluent reaction mixture from said alkylation zone into a catalyst phase and a hydrocarbon phase in a separation zone; recycling at least a portion of said catalyst phase to said alkylation zone; introducing said hydrocarbon phase into a fractionation zone, removing unreacted hydrocarbons previously associated with the olefin-aromatic containing fraction; mixing resulting high-boiling alkylate material with a molar excess of benzene in a mixing zone, contacting resulting mixture in a side-chain transfer zone with a liquid type alkylation catalyst; maintaining temperature in said side-chain transfer zone in a range of 60 to 140° F.; maintaining a pressure in said side-chain transfer zone sufficient to prevent vaporization of the catalyst; maintaining a volume ratio of catalyst to total hydrocarbon material in said side-chain transfer zone in range of 1:1 to 1:5; maintaining a rate of flow of reactants and catalyst such that residence time in said side-chain transfer zone is in range of 20 to 60 minutes; separating effluent reaction mixture from said side-chain transfer zone into a catalyst phase and a hydrocarbon phase in a separating zone; recycling at least a portion of said catalyst phase to said side-chain transfer zone and remaining catalyst phase to said alkylation zone; introducing said hydrocarbon phase into a fractionation zone and removing unreacted benzene from said hydrocarbon phase; introducing remaining hydrocarbon phase into a second fractionation zone, removing low-boiling aromatic constituents resulting from the side-chain transfer reaction in said transfer zone, introducing resulting high-boiling alkyl benzene material into a third fractionation zone and removing monoalkyl benzenes as a product of the process.

4. A two-step process for catalytically producing high molecular weight alkyl benzenes, which comprises catalytically cracking a high-boiling naphtha by mixing the naphtha with preheated steam and passing the mixture at a temperature in the range 950 to 1050° F. at a pres-

sure of 75 to 100 pounds per square inch gauge over a fixed bed, alumina type catalyst, fractionating the resulting cracked naphtha to produce a fraction containing olefins having at least seven and not more than eighteen carbon atoms to the molecule and alkylatable aromatic constituents; contacting said fraction with a liquid type alkylation catalyst in an alkylation zone; maintaining the temperature in said alkylation zone in the range of 60 to 140° F.; maintaining pressure in said alkylation zone sufficient to prevent vaporization of said catalyst; maintaining a volume ratio of catalyst to said fraction in alkylation zone in the range of 1:1 to 1:5; maintaining a rate of flow of said fraction and catalyst such that the residence time in said alkylation zone is in the range of 5 to 40 minutes; separating effluent reaction mixture from said alkylation zone into a catalyst phase and a hydrocarbon phase in a separation zone; recycling at least a portion of said catalyst phase to said alkylation zone; introducing said hydrocarbon phase into a fractionation zone, removing unreacted hydrocarbons previously associated with the olefin-aromatic containing fraction; mixing resulting high-boiling alkylate material with a molar excess of benzene in a mixing zone, contacting resulting mixture in a side-chain transfer zone with a liquid type alkylation catalyst; maintaining temperature in said side-chain transfer zone in the range of 60° to 140° F.; maintaining the pressure in said side-chain transfer zone sufficient to prevent vaporization of catalyst; maintaining a volume ratio of catalyst to total hydrocarbon material in said side-chain transfer zone in the range of 1:1 to 1:5, maintaining the rate of flow of reactants and catalyst such that residence time in said side-chain transfer zone is in the range of 20 to 60 minutes; separating effluent reaction mixture from said side-chain transfer zone into a catalyst phase and a hydrocarbon phase in a separating zone; recycling at least a portion of said catalyst phase to said side-chain transfer zone and remaining catalyst phase to said alkylation zone; introducing said hydrocarbon phase into a debenzenizing zone and removing unreacted benzene from said hydrocarbon phase; introducing remaining hydrocarbon phase into a fractionation zone, removing low-boiling aromatic constituents resulting from the side-chain transfer reaction in said transfer zone, introducing resulting high-boiling alkyl benzene material into a second fractionation zone and removing monoalkyl benzenes as a product of the process.

5. A process as in claim 4 wherein the catalyst used is anhydrous hydrogen fluoride.

6. A process as in claim 4 wherein the catalyst is a boron fluoride complex.

7. A process as in claim 4 wherein the catalyst used is hydrofluoric acid of at least 50 per cent concentration.

WALTER A. SCHULZE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,001,907	Ipatieff	May 21, 1935
2,315,506	Danner et al.	Apr. 6, 1943
2,343,870	Kaplan	Mar. 14, 1944
2,349,211	Tulleners	May 16, 1944

(Other references on following page)

UNITED STATES PATENTS

Number	Name	Date
2,376,119	Bruner et al.	May 15, 1945
2,385,524	Mattox	Sept. 25, 1945
2,396,682	Carmody	Mar. 19, 1946
2,403,879	Schulze et al.	July 9, 1946
2,413,161	Zerner et al.	Dec. 24, 1946
2,456,119	Friedman et al.	Dec. 14, 1948

OTHER REFERENCES

Simons, "Potential Use . . . Processes," Ind. and Eng. Chem., vol. 32, No. 2 (Feb. 1940), pages 178-183 (6 pages).
Schulze et al., "Gas-Oil . . . Cycloversion Process," Oil and Gas Jour., vol. 42 (April 13, 1944), pages 225, 6, 9, 30, 35 (5 pages).