RESERVE COPY

PATENT SPECIFICATION

3525

585,352

Convention Date (United States of America): Oct. 17, 1942.

Application Date (in United Kingdom): Sept. 9, 1943. *No. 14840/43.*

Complete Specification Accepted: Feb. 5, 1947.

(Under Section 6 (1) (a) of the Patents &c. (Emergency) Act, 1939, the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1942, became operative on Jan. 1, 1946).

COMPLETE SPECIFICATION

Production of Motor Fuel and Aromatic Hydrocarbons from Fischer Synthesised Hydrocarbon Oils

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention is directed toward the production of automotive fuel and, more particularly, it relates to a method of improving a hydrocarbon oil boiling in the naphtha and/or gas oil range, particularly as regards octane number, which naphtha or gas oil is of the Fischer type. By " Fischer " type naphtha or gas oil, we refer to hydrocarbons synthesized from CO and H_2 in the presence of a known suitable catalyst and under known conditions of temperature, pressure, etc.

As is generally known, hydrocarbons may be " Fischer " synthesized in the presence of suitable catalysts such as iron, nickel or cobalt either alone or deposited on a carrier such as kieselguhr or kaolin. This may be promoted and stabilized by alkalies and manganese and copper. These products, however, have a very low octane number since they are largely composed of normal paraffins. It is known to hydroform such " Fischer " hydrocarbons in the presence of a suitable catalyst for the production of benzene and its homologues.

It has now been found that valuable motor fuels and aromatic hydrocarbons may be prepared simultaneously from " Fischer " hydrocarbons, by a preliminary fractionation into two fractions boiling within the naphtha range and the gas oil range respectively, followed by hydro-forming the naphtha fraction, and catalytic cracking of the gas oil fraction, further fractionating the hydroformed and cracked fractions into a light fraction, a heavy fraction, and an intermediate fraction rich in aromatics, and combining the two light fractions and the two heavy fractions to form a gasoline. Aromatic hydrocarbons may be recovered from one or both of the intermediate fractions.

Thus the present invention comprises a process for the production of motor fuels and aromatic hydrocarbons from " Fischer " synthesised hydrocarbons, wherein the said " Fischer " hydrocarbons are fractionated into two fractions boiling within the naphtha range and the gas oil range respectively, the naphtha fraction being then catalytically hydroformed, and the products of the hydroforming reaction being further fractionated into a light fraction, a heavy fraction and an intermediate fraction rich in aromatic hydrocarbons, and the gas oil fraction being catalytically cracked, a fraction boiling within the gasoline range being separated from the cracked products and further fractionated into a light fraction, a heavy fraction and an intermediate fraction rich in aromatic hydrocarbons, and the aromatic hydrocarbons being separated by solvent extraction from one or both fractions rich in aromatics hydrocarbons, and the said light and heavy fractions being blended to form a gasoline.

In this way there may be produced simultaneously a motor fuel having a high octane rating and substantially pure aromatic hydrocarbons, e.g. toluene of so called " nitration grade ".

The hydroforming operation in itself is well known and normally consists in subjecting the oil to temperatures between 800 and 1000° F. at pressures of 100—400 lbs/sq. and in the presence of a hydroforming catalyst, such as chromia or molybdena alone or supported on activated alumina, or other VI Group oxide or a mixture of sulfides, such as nickel and tungsten sulfides, and also employed in the presence of added hydrogen. The hydroforming operation is, for the most

[*Price* 1/-]

Price 3s. 6d.

Price 25p

part, one of dehydrogenation with the formation of aromatics and olefins from paraffins, accompanied also by some cyclization of paraffins, aromatization, isomerization and cracking of paraffins, but the operation generally is conducted under conditions such that there is a minimum change in the boiling range of the charging oil.

In the accompanying drawing, we have indicated diagrammatically a flow plan illustrating a preferred modification of our invention.

Referring to the drawing for a better understanding of our invention, a Fischer synthetic hydrocarbon is introduced into the present system through line (1) and thence distilled in a fractionator (3) into an overhead fraction boiling within the range of from 123—424° F., which fraction is withdrawn through line (5), condensed in a cooler (7) and thence discharged through line (8) into a naphtha storage vessel (10).

The bottoms from distillation zone (3) and boiling say from 440—650° F. are withdrawn through line (15), condensed in a cooler (17), thence discharged through line (19), into a gas oil storage vessel (20).

The overhead fraction and the gas oil bottoms from the distillation zone (3) are treated as will be more fully explained hereinafter. At the outset it is explained that the naphtha is subjected to hydroforming, while the gas oil is cracked. The hydroforming operation results in the production of aromatics which may be solvent extracted to recover, for example, toluene with a degree of purity suitable for nitration. The gas oil cracking also results in the production of an automotive fuel of high octane number, together with toluene of a high degree of purity.

Continuing the description of the process shown in the drawing, the naphtha in storage vessel (10) is withdrawn through a line (30) and thence discharged into a heater (32), which may be a furnace or other suitable heating means, where it is heated to reaction conditions, thence discharged through line (35) into a reactor (40) containing a catalyst of the type previously indicated. Hydrogen from (50) is withdrawn through line (52), heated in a fired coil or other heating means (53), and thence discharged through line (55) into reactor (40) so it is present with the oil undergoing treatment. With respect to operating conditions, the following give good results:

Temperature	850—1000° F., with temperatures of from about 925—950° F preferred.
Pressure	From 150—400 lbs. per sq. in. gauge, with about 250 lbs. pressure preferred.
Feed Rate of Oil	From 0.5—2 volumes of oil per volume of catalyst per hour on a cold oil basis, with a feed rate of about 1.2 volumes of oil per volume of catalyst per hour preferred.

Hydrogen proportion is in the range of from say 2000—4000 cubic feet per barrel of cold oil.

Under these conditions the naphtha undergoes reforming, and the reformed products are withdrawn through line (60) and discharged through a cooler (62), and thence discharged through line (64) into a separation drum (70). Overhead from separation drum (70) a hydrogen-enriched gas is withdrawn through line (72) and pumped by pump (75) to hydrogen storage vessel (50) for further use in the process.

The bottoms from the separation drum (70) are withdrawn through line (80) and discharged into fractionator (85) from which several fractions are recovered as follows: First, an overhead fraction boiling within the range of from about 130—210° F. and representing about 44 volume per cent of the oil in line (80) is withdrawn through line (88) and discharged after cooling into condenser (90) and thence into a gasoline storage vessel (100). The bottoms fraction representing about 39 volume per cent of the product fed to the fractionator (85) is withdrawn through line (95), condensed in a cooler (97) and thence discharged into line (88), where it mixes with the lighter ends from the fractionator and flows with the latter into gasoline storage vessel (100). Thus from the hydroforming operation, the lighter and heavier ends are recovered as gasoline blending agents.

Referring again to fractionator (85), a side cut representing about 17% of material charged to (85) and boiling within the range of from about 210—250° F. is withdrawn as a side stream through line (99). This fraction is purified by solvent treatment although other auxiliary means may be employed. Thus, for example, this fraction contains normally not only the toluene, but also paraffins boiling within the range of 210—250° F. and a minor amount of olefins also boiling within this range, although the presence of hydrogen tends to saturate olefins formed in reactor (40), so that the final result of the reforming operation is to produce paraffins and aromatics. In the drawing we have shown solvent extraction employing SO_2 as the selective solvent for the aromatics. Towards this end, the SO_2 is withdrawn from the source (110) and discharged into the top of solvent extraction vessel (115) where it flows countercurrently to the hydrocarbon oil fraction entering from (99). As a further aid to the process, a paraffinic wash solvent such as pentane is withdrawn from the storage vessel (120) and discharged through line (122) into solvent extraction tower (115). Of course, in solvent extraction tower (115) the usual formation of raffinate and extract phases takes place. The raffinate phase is withdrawn through line (130) and discharged into a stripping tower (135). This raffinate is stripped to remove the SO_2 which is withdrawn through line (140) and pumped by pump (142) to storage vessel (110). The bottoms from stripper (135) are withdrawn through line (145) and discharged into fractionating column (147). The overhead fraction comprising the paraffinic wash solvent is withdrawn from the fractionator (147) through line (149), condensed in condenser (150), thence pumped back through line (151) to the paraffin storage (120). The bottoms from fractionator (147) are withdrawn through line (155) and discharged into line (157) leading to gasoline storage vessel (100). The bottoms withdrawn from fractionator (147) through line (155) may be discharged through line (156) to either the hydroforming zone (40) or the cracking zone (320).

As previously indicated, there is an extract phase formed in extraction vessel (115) and this is withdrawn through line (160) and discharged into stripper (162) where the solvent is removed by distillation, withdrawn through line (163) and pumped by pump (164) into storage vessel (110). The substantially solvent-free extract is withdrawn from stripper (162) through line (170) and discharged into a fractionating column (175). The paraffins still remaining or associated with the toluene cut are withdrawn through line (180), condensed in a condenser (182) and thence discharged through line (183) into paraffinic wash solvent storage (120). The toluene is recovered from fractionator (175) through line (190) and thence discharged into an acid treating vessel (192) where it is treated preferably with sulfuric acid of polymerizing strength, such as about 65% by weight, or it may be treated with a polymerizing clay to polymerize the olefins to convert them to heavier polymers which may be separated from the toluene by distillation. The thus treated material is withdrawn through line (195) and discharged into fractionator (200) from which lighter ends may be withdrawn through line (210), while the heavier polymers are withdrawn through line (212). The desired toluene is withdrawn as a side stream through line (205) and delivered into a toluene storage vessel (208). The toluene in (208) has a degree of purity sufficient for making trinitrotoluene or any other product requiring a high degree of purity.

Referring to the heavy bottoms of the original Fischer product, it will be recalled that these were collected in storage drum (20). This material is to be subjected to catalytic cracking and towards this end it is withdrawn through line (300), discharged into a suitable fired coil or other heating means (310) where it is heated to cracking temperatures, say from 825—925° F. and thence withdrawn through line (312) and discharged into a catalytic cracking reactor (320) where it contacts a cracking catalyst such as an acid treated montmorillonite clay or a synthetic cracking catalyst consisting of silica and alumina or silica and magnesia. The catalysts, as well as cracking conditions for this operation are known to the art. Normally good results are obtained by operating at a temperature of 875° F. and at a relatively low pressure and permitting contact between the catalyst and oil vapors at reaction temperatures of from 15—25 seconds or more. Under these conditions the gas oil undergoes cracking to form catalytically cracked gasoline in good yields thereof amounting to 35—40%. The cracked products are withdrawn through line (330) and discharged into fractionating column (335). Unconverted gas oil is withdrawn from fractionator (335) through line (340) and thence discharged into storage vessel (20) for further treatment. However, a portion of this oil is head from fractionator (335) through line (342), particularly as it becomes increasingly refractory, and the thus withdrawn oil may be used for a heating oil or for some other purpose. The normally gaseous constituents are withdrawn overhead from fractionator (335) through line (350). These gases contain butylene, isobutylene, normal butane and isobutane and they may be processed in means not illustrated to form by alkylation branch chain hydrocarbons boiling within the gasoline range, or they may be converted to synthetic rubber intermediates such as butadiene, or otherwise disposed of.

A fraction boiling within the range of from 100—400° F. is withdrawn from fractionator (335) through line (360) and discharged into a fractionating column

(370). The product entering (370) is divided into three fractions as follows: first, an overhead fraction containing the lighter ends which is withdrawn through line (380) and condensed in a cooler (381) and thence discharged into stream (88) where it flows with the overhead from the hydroforming operation into gasoline storage vessel (100). The bottoms from fractionator (370) may be withdrawn through line (390), condensed in cooler (391) and also discharged into gasoline storage vessel (100). Finally, an intermediate cut boiling from 210—250° F. and representing about 10% of the material discharged into fractionator (370) is withdrawn as a side stream through line (400), nd this may be discharged into line (99) to recover with the product from the hydroforming operation, its toluene content, in a manner which has already been described.

In an alternative modification, the intermediate cut boiling from 210—250° F. which is withdrawn from fractionator (370) through line (400) may be discharged into line (153) for ultimate reforming in zone (40) or passed through lines (156) and (305) to coil (310) and thereafter cracked.

We have shown solvent extracting a toluene fraction with liquid sulfur dioxide. Instead of using this method, we may use another solvent such as phenol, in which operation the vapors to be extracted are treated with liquefied anhydrous phenol. This process or the process of extracting with liquid SO_2 do not form *per se* the gist of our invention and any known method for recovering toluene by solvent extraction may be employed. If the solvent is SO_2 the temperature maintained in the extraction zone (115) should be from 0 to −60° F. or lower. The flow of SO_2 with respect to the hydrocarbon should be from 1—3 parts by weight of SO_2 per weight of hydrocarbons and the volume of paraffinic wash solvent, for example, pentane from (120) should be from ½ to 1½ volumes of the wash solvent per volume of liquid consisting of SO_2 and the hydrocarbon in the extractor (115). Of course, it will be appreciated that in reactors (40) and (320) the reactions therein taking place result in the deposition of cokey or tarry deposits on the catalyst and these operations must be interrupted intermittently to remove these deposits since they deactivate the catalyst. This can be accomplished in known manner by burning off the tarry or cokey deposits with an oxygen-containing gas.

In the foregoing disclosure, we have described our process in terms of fixed or stationary beds of catalyst. Our process may be carried out using a suitable powdered catalyst suspended in the reaction vapors in the several reaction zones. Thus, the hydroforming and/or cracking operations may be carried out by flowing the vapors to be cracked or reformed through a zone where they contact a fluidized powdered catalyst which is suspended in said vapors.

Also, of course, in the operations described there will come a time when it is necessary to regenerate the catalyst in the reaction zones. This may be accomplished, after discontinuing the flow of oil to the reaction zones, by treating the catalyst with an oxygen-containing gas, such as air, or air diluted with flue gas, at temperatures elevated sufficiently to cause burning of the fouling deposits. This procedure is well known in the art. Where the catalyst in powdered form moves in and out of the reactors, it may be regenerated in separate regeneration zones and thus render the operation continuous.

Another ramification of our process as herein described involves including the reproportionating of xylenes, formed during the reforming, with benzene in the presence of a suitable catalyst such as $AlCl_3$ whereby additional quantities of toluene may be produced. The details of this process are generally known in the prior art.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of motor fuels and aromatic hydrocarbons from "Fischer" synthesised hydrocarbons, wherein the said "Fischer" hydrocarbons are fractionated into two fractions boiling within the naphtha range and the gas oil range respectively, the naphtha fraction being then catalytically hydroformed, and the products of the hydroforming reaction being further fractionated into a light fraction, a heavy fraction and an intermediate fraction rich in aromatic hydrocarbons, and the gas oil fraction being catalytically cracked, a fraction boiling within the gasoline range being separated from the cracked products, and further fractionated into a light fraction, a heavy fraction and an intermediate fraction rich in aromatic hydrocarbons, and the aromatic hydrocarbons being separated by solvent extraction from one or both fractions rich in aromatic hydrocarbons, and the said light and heavy fractions being blended to form a gasoline.

2. A process according to Claim 1, wherein the hydroforming reaction is carried out at a temperature between 800° and 1000° F. and preferably at a temperature between 925° and 950° F.

3. A process according to Claim 2, wherein the hydroforming reaction is carried out at a pressure between 100 and 400 lbs./sq. inch, and preferably 250 lbs./sq. inch.

4. A process according to any of the preceding Claims, wherein the catalyst employed in the hydroforming reaction is chromia, or molybdena, either alone or supported on activated alumina, or a mixture of metallic sulfides.

5. A process according to any of Claims 2 to 4, wherein the feed rate of the naphtha fraction into the hydroforming step is between 0.5 and 2 vols. of oil per vol. of catalyst per hour on a cold oil basis with a preferred rate of 1.2 vols. per hour.

6. A process according to any of Claims 2 to 5, wherein the hydrogen added in the hydroforming process is between 2000 and 4000 cu. ft. per barrel of said naphtha fraction.

7. A process according to any of the preceding Claims, wherein the said cracking reaction is conducted at a temperature between 825° and 925° F., preferably 875° F.

8. A process according to Claim 7, wherein the cracking catalyst is an acid-treated clay or a synthetic silica-alumina.

9. A process according to Claims 7 or 8, wherein the vapors of the said gas oil fraction are in contact with the cracking catalyst for from 15—25 seconds.

10. A process according to any of the preceding Claims, wherein the said second named intermediate fraction rich in aromatic hydrocarbons is blended with the naphtha fraction forming the feed stock for the hydroforming treatment.

11. A process according to any of Claims 1 to 9, wherein the said second named intermediate fraction rich in aromatic hydrocarbons is recycled for further catalytic cracking.

12. A process according to any of the preceding Claims, wherein toluene is solvent-extracted from the said fraction or fractions rich in aromatic hydrocarbons.

13. A process according to any of the preceding Claims, wherein the solvent employed is liquid sulfur dioxide or phenol.

14. A process according to any of the preceding Claims, wherein the amount of toluene in the said fraction or fractions rich in aromatic hydrocarbons is increased by reproportionating the xylenes and benzene formed in the hydroforming reaction to form additional toluene.

15. A process according to any of the preceding Claims, wherein the said naphtha fraction boils within the range of 123°—424° F., the said gas oil fraction boils within the range or 440°—650° F., the boiling range of the fractions from the hydroformed naphtha fraction are within the ranges 130°—210° F., 210°—250° F., and 250° F. to the end point of the said fraction, the boiling range of the fraction boiling within the gasoline range separated from the cracked products being from 100°—400° F., and the boiling range of the fractions separated from said last fraction being from 100°—210° F., 210°—250° F., and 250°—400° F. respectively.

16. A process for the production of motor fuels and aromatic hydrocarbons from "Fischer" synthesised hydrocarbons as herein described.

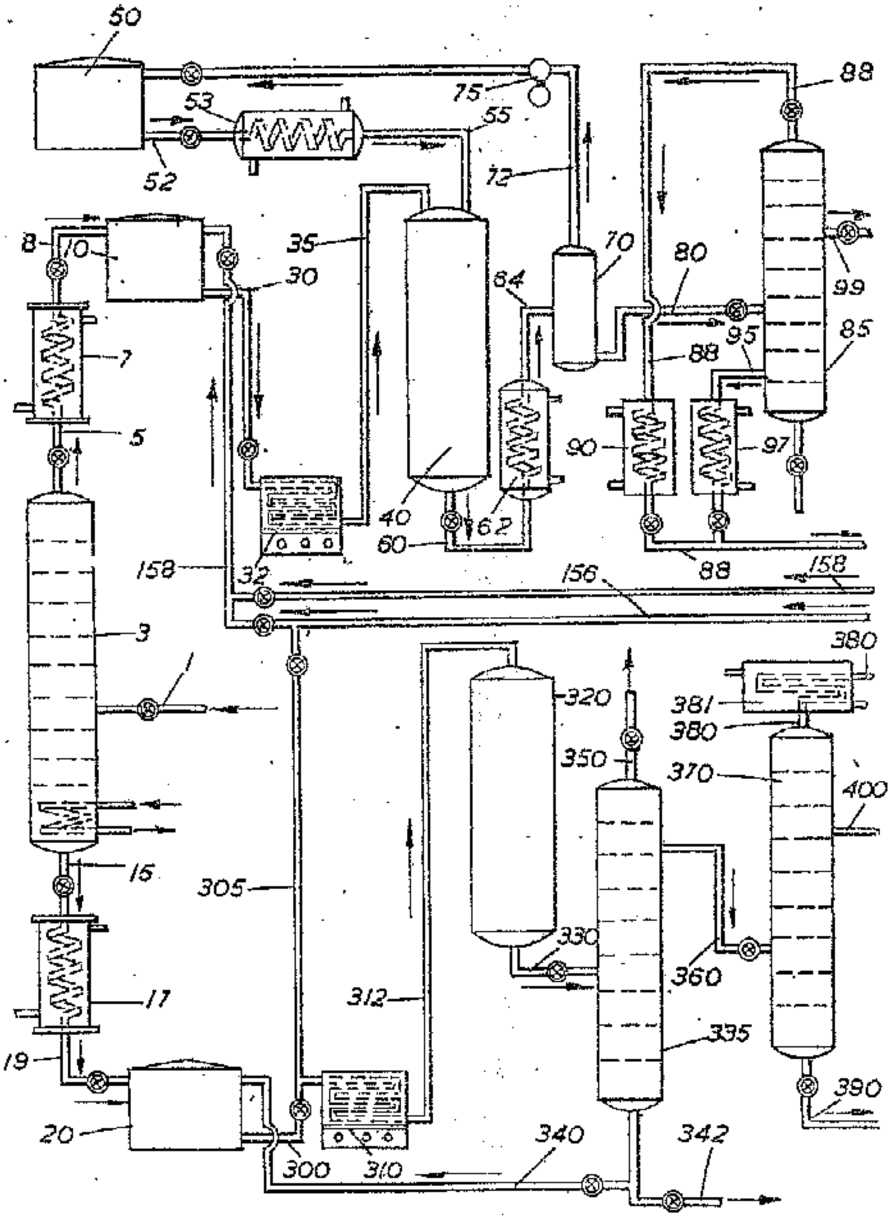
Dated this 9th day of September, 1943.

D. YOUNG & CO.,
29, Southampton Buildings,
Chancery Lane, London, W.C.2.
Agents for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1947.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.

[This Drawing is a reproduction of the Original on a reduced scale.]

FIG. 1.



SHEET 1

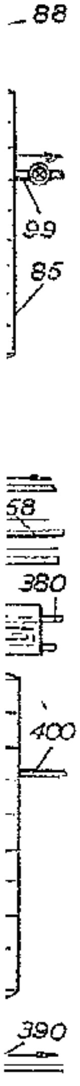
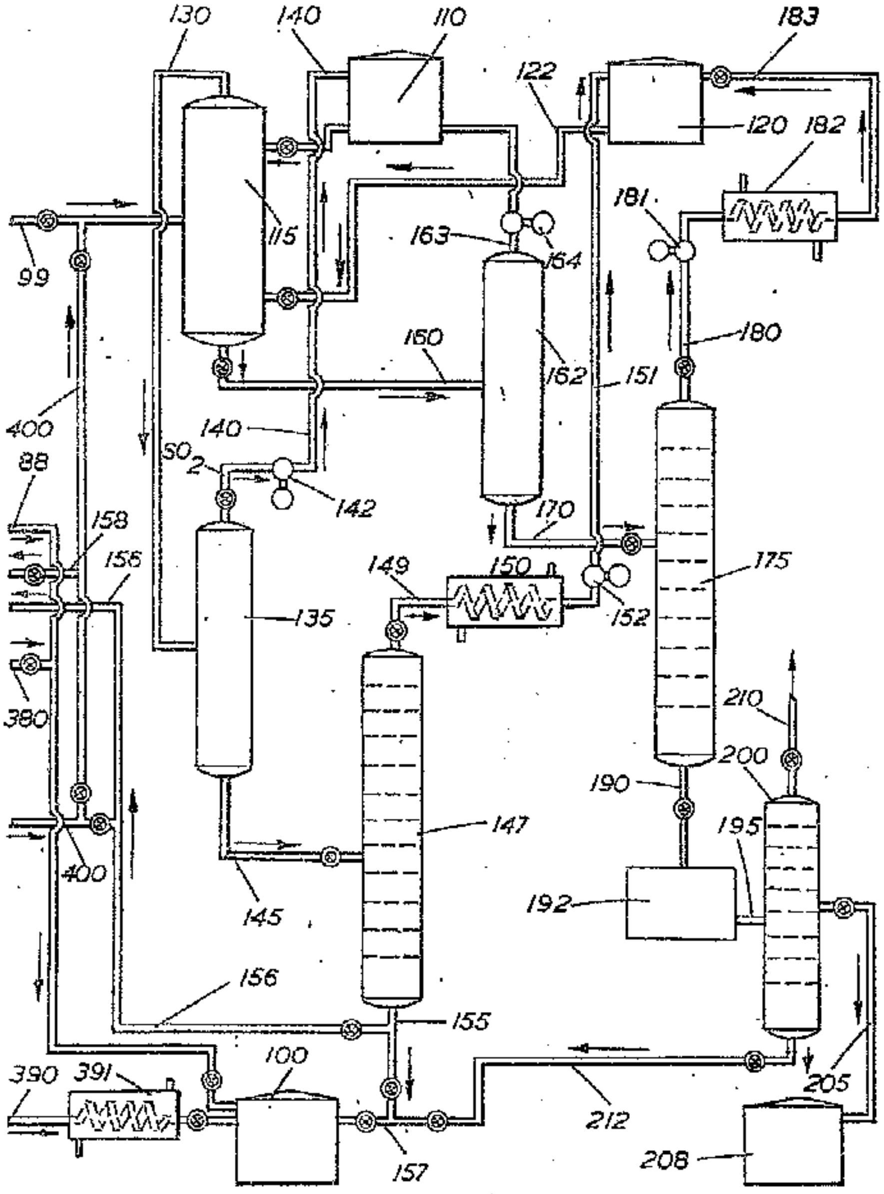


FIG. 1A.



[This Drawing is a reproduction of the Original on a reduced scale.]

FIG. 1.

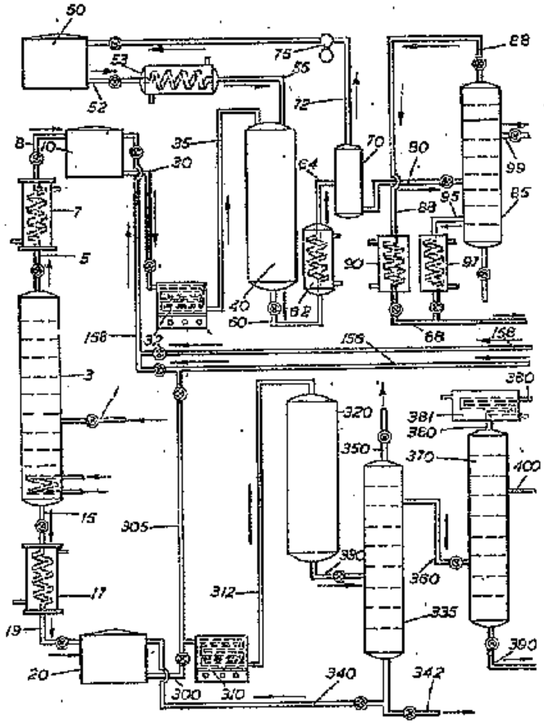


FIG. 1A.