Aug. 13, 1946. N. F. LINN 2,405,660

METHOD OF PRODUCING TOLUENE

Filed Oct. 17, 1942 2 Sheets-Sheet 1

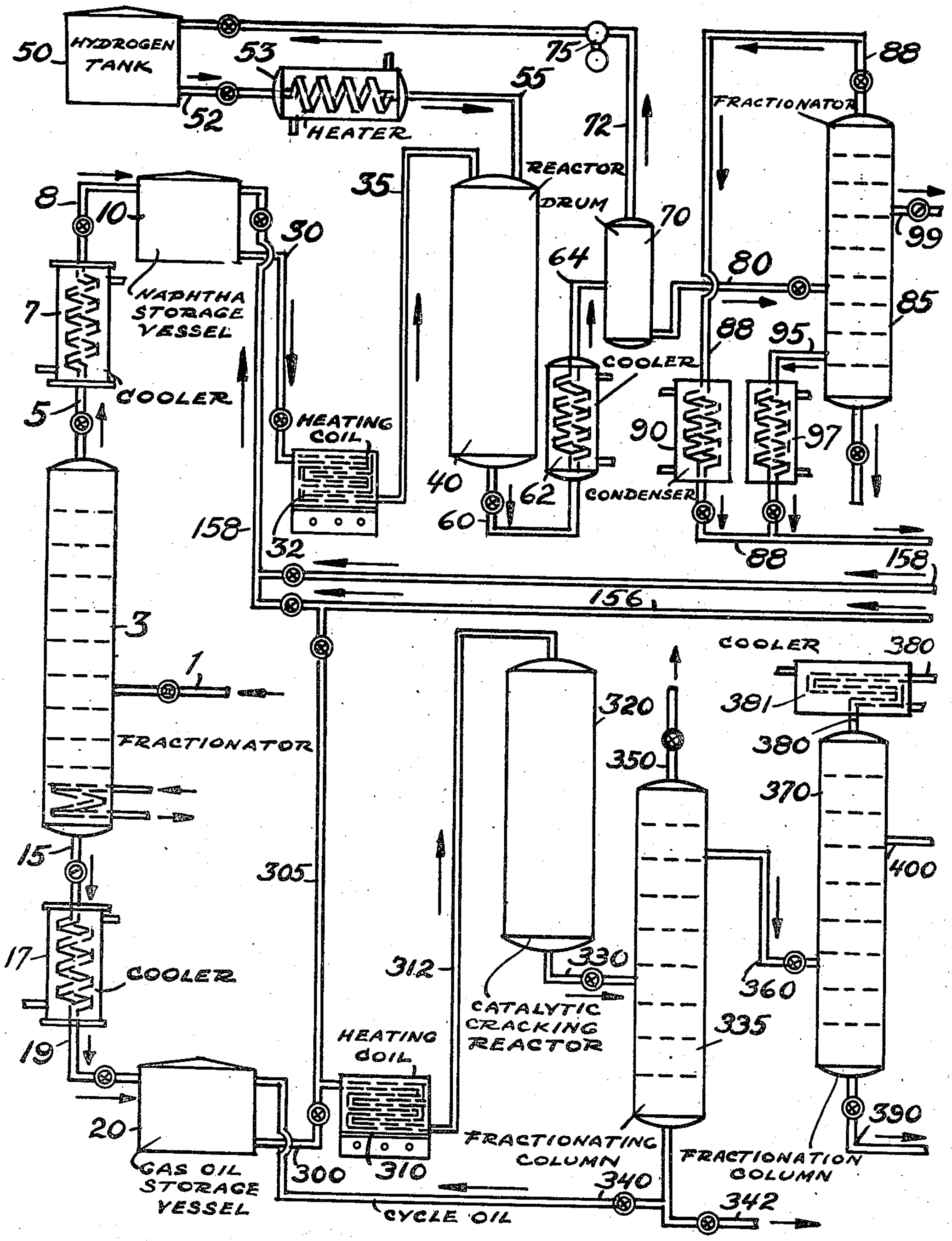

FIG. -1

Norman F. Linn Inventor

By P. L. Young Attorney

Aug. 13, 1946. N. F. LINN **2,405,660**

METHOD OF PRODUCING TOLUENE

Filed Oct. 17, 1942 2 Sheets-Sheet 2

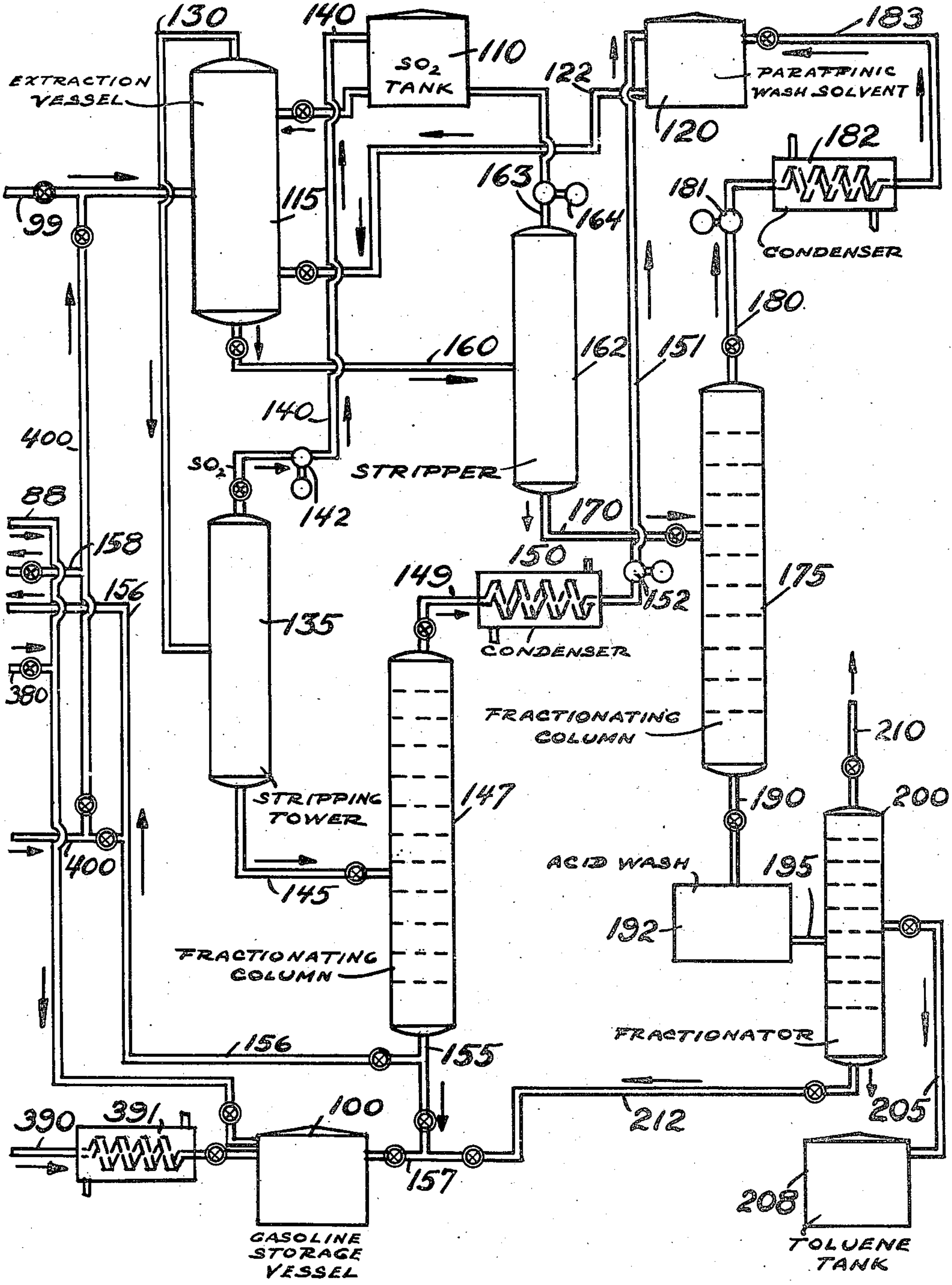

FIG.-1A

Norman F. Linn Inventor

By P. L. Young Attorney

Patented Aug. 13, 1946 **2,405,660**

UNITED STATES PATENT OFFICE

2,405,660

METHOD OF PRODUCING TOLUENE

Norman F. Linn, Mountainside, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

Application October 17, 1942, Serial No. 462,323

3 Claims. (Cl. 260—673.5)

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, I 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. Broadly speaking, my invention comprises improving the octane rating of such a hydrocarbon oil by subjecting it to a combined hydroforming, solvent extracting and catalytic cracking operation. It is also concerned with the production of substantially pure aromatics, e. g. toluene of so-called "nitration grade" by subjecting selected fractions to a combination of processes which will be more completely described below. By "hydroforming" I mean to imply an operation in which the treated oil is subjected to elevated temperatures, say of the order of 900–1000° F. and pressures of 100–400 lbs. per square inch and in the presence of a catalyst, 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 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 drawings, I have indicated diagrammatically a flow plan illustrating a preferred modification of my invention.

Referring to the drawings for a better understanding of my 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 reforming in the presence of hydrogen, while the gas oil is cracked. The reforming 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 drawings, 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 reforming 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, preferably, although other 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. As indicated, these paraffins in the boiling range of from 210–250° F. may be removed, for instance, by cracking them to products which will boil lower than the toluene so that after cracking, the toluene may be separated by simple distillation. In the drawings, however, I have shown solvent treating employing SO_2 as the selective solvent for the aromatics. Toward 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 reforming 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 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 withdrawn continuously 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 preferably 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 reforming 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**, and this may be discharged into line **99** to recover with the product from the reforming operation, its toluene content, in a manner which has already been described.

In an alternate modification, the intermediate cut boiling from 210–250° F. which is withdrawn from fractionator **370** through line **400** may be discharged into line **158** for ultimate reforming in zone **40** or passed through lines **156** and **305** to coil **310** and thereafter cracked.

Many modifications of the invention as above set forth may be made without departing from the spirit thereof. I have shown solvent extracting a toluene fraction with liquid sulfur dioxide. Instead of using this method, I 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 the liquid SO_2 do not form per se the gist of my 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, I have described my process in terms of fixed or stationary beds of catalyst. My process may be carried out using a suitable powdered catalyst suspended in the reaction vapors in the several reaction zones. Thus, the reforming 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 my 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.

What I claim is:

1. A method of producing toluene of high purity from a hydrocarbon product obtained by the hydrogenation of carbon monoxide which comprises fractionating the said hydrocarbon product into a naphtha fraction and a gas oil fraction, submitting the latter to a cracking treatment at a temperature of the order of 825–925° F. in the presence of a catalyst suitable for promoting the cracking of aliphatic hydrocarbons, recovering a fraction boiling at about 210° to about 250° F. from the product of said cracking treatment, combining such fraction with the naphtha fraction obtained in the fractionation of the product of the hydrogenation of carbon monoxide, subjecting the combined fractions to a reforming treatment at a temperature of the order of 850–1000° F. and under a pressure of the order of 100–400 lbs./sq. in. in the presence of hydrogen and a catalyst comprising an oxide of a group VI metal, recovering from the product of said treatment a fraction boiling at about 210° to about 250° F. and treating such fraction to selectively separate therefrom its aromatic content.

2. A process according to claim 1 in which the aromatic content of the fraction produced in the reforming treatment is separated therefrom by extraction with a solvent, followed by treatment of the extract phase with a paraffinic hydrocarbon solvent lighter than the paraffinic hydrocarbon remaining in said extract phase to displace the latter, and distillation to remove the said lighter paraffinic hydrocarbon solvent from the aromatic hydrocarbon product.

3. A process according to claim 1 in which the aromatic content of the fraction produced in the reforming treatment is separated therefrom by extraction with a solvent, followed by treatment of the extract phase with pentane to displace the paraffinic hydrocarbon remaining in said extract phase, and distillation to remove the pentane from the aromatic hydrocarbon product.

NORMAN F. LINN.