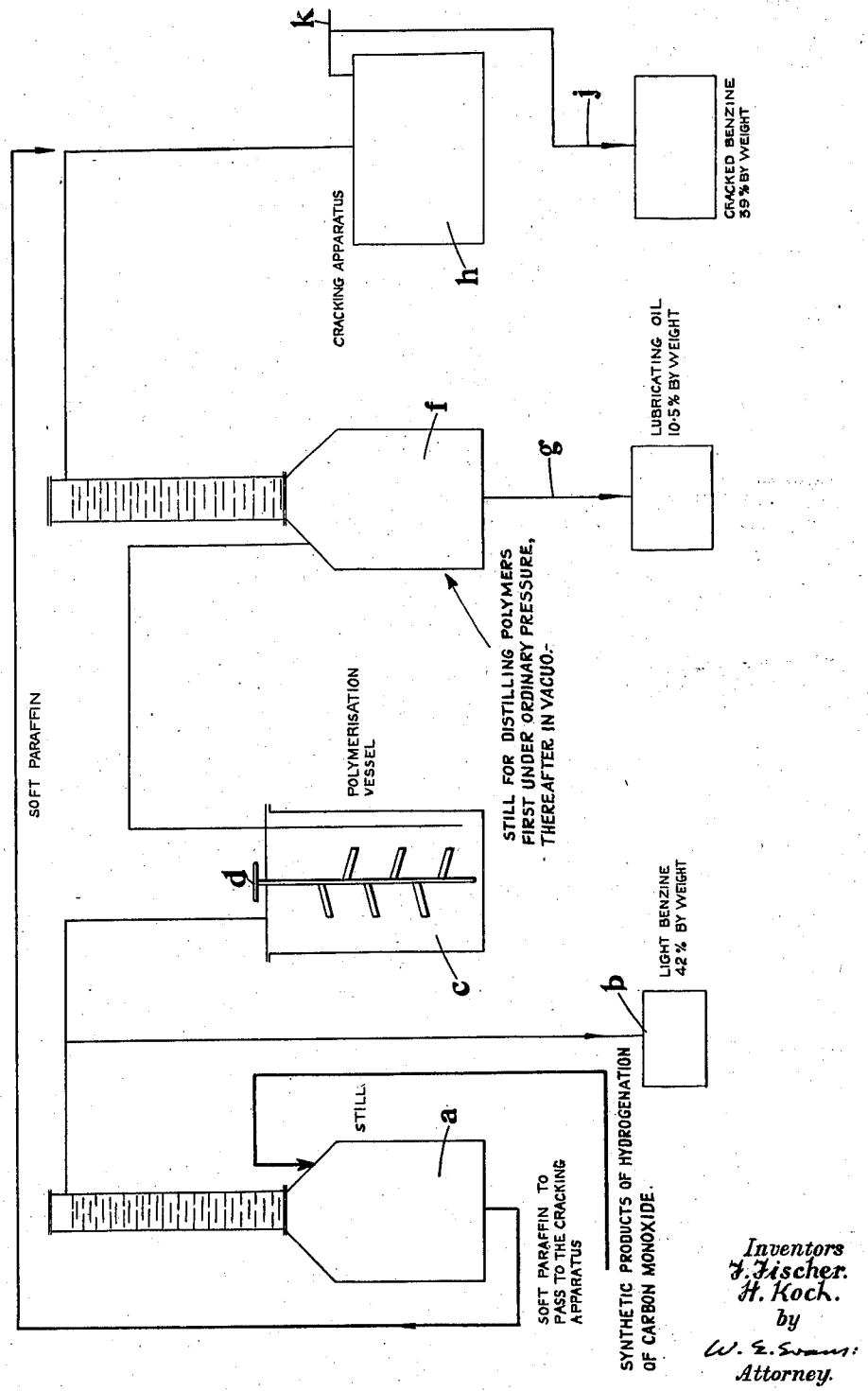
Sept. 6, 1938. F. FISCHER ET AL 2,128,994

PROCESS FOR TREATING SYNTHETIC BENZINE PRODUCTS FROM HYDROGEN AND THE OXIDES OF CARBON

Filed July 10, 1935



Inventors
F. Fischer.
H. Koch.
by
W. E. Evans.
Attorney.

Patented Sept. 6, 1938 2,128,994

UNITED STATES PATENT OFFICE

2,128,994

PROCESS FOR TREATING SYNTHETIC BENZINE PRODUCTS FROM HYDROGEN AND THE OXIDES OF CARBON

Franz Fischer and Herbert Koch, Mulheim-Ruhr, Germany, assignors to Studien- und Verwertungs-Gesellschaft mit beschrankter Haftung, Mulheim-Ruhr, Germany

Application July 10, 1935, Serial No. 30,624
In Germany July 19, 1934

2 Claims. (Cl. 196—50)

It is known that in the production of benzine by synthesis from carbon monoxide and hydrogen at normal pressure, as suggested for instance in Patent No. 1,746,464, gaseous and liquid aliphatic hydrocarbons are obtained having highly varying boiling points and comprising in addition to mono-olefines, mainly saturated hydrocarbons such as "gasol", light benzine, heavy benzine, illuminating oil, heating oil and solid paraffin, wherein "gasol" designates a mixture of gaseous saturated and unsaturated aliphatic hydrocarbons and more particularly a mixture of methane and ethane with their higher gaseous homologs. It is inherent in the nature of these products that from the benzines as obtained only the benzine which has a boiling point up to about 100° C. satisfies present day requirements in resistance to detonation, even when by selecting the conditions of production, the composition of the gases, and the nature of the catalyst are so determined that there are as many mono-olefines in the benzine as possible. On the other hand it has been found ("Brennstoffchemie" vol. 15 (1934) page 229), that particularly valuable lubricating oils can be produced by condensation from the mono-olefines of the fraction between 100 and 250° C. and over. In order to convert as far as possible the whole products of the synthesis of benzine into the particularly desirable substances, namely, anti-detonating benzine and valuable lubricating oils, it has been found particularly advantageous to proceed as follows:—

First of all light benzine which boils up to about 100° C. is removed from the liquid raw product obtained at normal pressure by the synthesis of benzine from hydrogen and the oxides of carbon. Thereupon solid paraffin is removed from the higher-boiling benzine either by distillation or in any other manner, for example by cooling or by solution or by fractional distillation. Lubricating oils having a low solidification point are obtained by condensation from the olefines contained in the higher boiling constituents either directly or after dilution or after an enriching operation. The production of the lubricating oils in this state is of importance, because before cracking no other constituents, such as aromatic hydrocarbons, are present. Due to the absence of aromatic hydrocarbons, lubricating oils are obtained in this manner, the viscosity of which is dependent upon the temperature in a rather small measure. Thereupon distillation is advantageously carried out under vacuum during which the lubricating oils remain behind. The distillate is subjected to a cracking process which can produce benzine that is resistant to detonation. The soft solid paraffin removed, as mentioned above, from the higher-boiling benzine before the production of the lubricating oil, may be admixed with the distillate separated from the lubricating oils and may thus be subjected to the same cracking process. The light benzine hereinbefore referred to and the cracked benzine produced may then be mixed in any suitable proportions or may be used separately, according to which kinds of benzine are desired. By this method the entire raw liquid products resulting from the synthesis of benzine can be treated to produce benzine resistant to detonation and valuable lubricating oils, in addition to a small residue of oil resulting from the cracking operation. This method produces primarily a light benzine whose resistance to detonation is equal to that of Baku benzine, while furthermore cracked benzines are obtained whose octane number is over 70, and finally the combined operations described produce valuable lubricating oils having viscosity indices lying between 1.6 and 2.6, whose absolute viscosity is merely a question of concentrating by distillation.

In carrying the invention into effect according to one method 100 kg. of a raw product are taken, produced at a reaction temperature of about 200° C. from water gas at normal pressure by the use of a catalyst consisting of cobalt metal and zinc oxide. The water-clear product has a specific gravity of 0.72 at 20° C., and consists up to about 45% of olefine hydrocarbons. At first the mixture is distilled at normal pressure until the temperature of the vapor is 125° C. By this means 42 kg. of light benzine is obtained which has a specific gravity of 0.67 at 20° C., and has an olefine content of 60% by volume. The octane number determined by the C. F. R. motor method is 65. The distillation of the raw product is then continued until the temperature of the vapor is 250° C., 37 kg. of a heavy benzine distillate being secured. The residue of distillation amounting to 21 kg., by reason of the high content of soft paraffin, solidifies to produce crude paraffin.

The heavy benzine distillate of a specific gravity of 0.74 has an olefine content of 40%, and is treated in the manner hereinafter described to produce lubricating oil.

The product is first mixed in an iron polymerization vessel provided with a good stirrer, with 1 kg. of commercial anhydrous aluminium

chloride at room temperature, whereupon the reaction temperature is raised within a period of 2 hours to 120° C. At this temperature the mixture is well stirred for a further six hours, and then allowed to cool. The reaction product is as the result separated into two layers, the lower of which consists of an addition-compound of aluminium chloride which can be used as catalyst for further conversions. To secure lubricating oil the upper layer of oil is first purified with about 1% of fuller's earth and then is subjected to distillation. The distillation is carried out until the vapor temperature is 250° C. at normal pressure, and then is continued under vacuum at 15 mm. of mercury, until the vapor temperature is 200° C. This produces 25 kg. of a distillate, and as residue 10.5 kg. of a lubricating oil having the following properties:

Specific gravity at 20° C. 0.840; viscosity 20.8° Engler at 20° C. and 4.66° Engler at 50° C; viscosity index 1.90; solidification points —36° C. The distillate contains practically no olefine hydrocarbons, and is cracked for conversion into anti-knock benzine together with soft paraffin which is left in distilling the raw product which serves as raw material for the process.

The residue which contains soft paraffin to the extent of 21 kg. and the distillate poor in olefines originating from the manufacture of lubricating oil to the extent of 25 kg. produce during combined cracking 39 kg. of a cracked benzine whose octane number is 75.

Thus by treating the raw product of synthetic benzine by the process according to the present invention 42% by weight of primary benzine is produced having octane number 65, 39% by weight of cracked benzine, having octane number 75, and 10.5% by weight of valuable lubricating oil with a viscosity index of 1.90.

The process of the invention is diagrammatically indicated by way of example in the accompanying drawing. As illustrated in the drawing the raw product which is obtained in the synthesis of benzine from carbon monoxide and hydrogen at normal pressure is first distilled off in the still *a* up to a temperature of 125° C. of the vapors passing off. These vapors provide during condensation a light benzine *b* which is sufficiently resistant to detonation. Thereupon the residue in the still *a* is further distilled until a vapor temperature of 250° C. is reached. The heavy benzines produced, after condensation pass into the polymerization vessel *c* which is provided with a stirring device *d*. The raw product obtained during polymerization is carried over into the still *f* and then distilled. A lubricating oil remains which is drawn off at *g* while the distillate passes into the cracking apparatus *h*. Furthermore the soft paraffins remaining behind in the still *a* after the second distillation are passed into the cracking apparatus *h*. The remaining cracked benzine is drawn off at *j* while the uncondensed cracking gases leave at *k*.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

We claim:

1. The method of converting into more valuable products synthetic benzine obtained by reacting hydrogen with carbon monoxide in the presence of a catalyst at elevated temperature under about atmospheric pressure, comprising the steps of subjecting the product of the reaction of hydrogen with carbon monoxide, from which have been separated the fraction boiling below 100° C. and the paraffin capable of solidification, which was formed in said reaction, to polymerization in the presence of a polymerization catalyst, of thereafter distilling the polymerization product first at ordinary pressure and then in vacuo for the recovery of a residue adapted for use as a lubricant and of a further quantity of low-boiling benzine, of admixing said paraffin to this low-boiling benzine and of cracking said mixture for the recovery of knock-proof benzine.

2. The process of producing knock-proof benzine and lubricating oil, which comprises passing watergas at about 200° C. and at about atmospheric pressure in contact with a hydrogenation catalyst, subjecting the reaction products to distillation at a temperature up to about 125° C., separating the distillate, continuing distillation up to about 250° C., heating the second distillate, after separation from the paraffinic residue obtained, under stirring in the presence of a polymerization catalyst to about 120° C., purifying the oil layer thereby obtained, distilling same at ordinary pressure up to 250° C., and continuing the distillation up to 200° C. under a high vacuum for the recovery of a third distillate and of a residue which is adapted for use as a lubricant, and cracking said third distillate together with said paraffinic residue to recover knock-proof benzine.

FRANZ FISCHER.
HERBERT KOCH.