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(54) WORKING UP OF PRODUCTS FROM THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

(54) PREPARATION DE PRODUITS D'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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This invention relates to improvements in the working up of products from the catalytic hydrogenation of carbon monoxide.

As is well known, synthesis products which boil within wide limits are obtained from catalytic carbon monoxide hydrogenation depending upon the synthesis conditions and the catalysts used. As reaction products flow from the reactors, at first the liquid high boiling hydrocarbon mixtures are separated. These liquid high boiling hydrocarbon mixtures are termed the "reactor paraffins".

After the separation of these reactor paraffins, the temperature of the reactor gas is decreased to about 100°C, as, for example, with the use of heat exchangers. As a result of this cooling a condensate is obtained and recovered which is termed the "heat exchanger condensate".

After removal of the "heat exchanger condensate", the gas is further cooled to normal room temperature which results in the formation and recovery of the so-called "cold condensate".

The gases remaining after the removal of the "cold condensate" are subjected to an oil scrubbing or to cooling to temperatures as low as -40°C. or to suitable treatment with active carbon for recovery of the "low temperature condensate".

It is often desirable to obtain as large a quantity as is possible of motor fuels from the catalytic hydrogenation of carbon monoxide. In order to obtain these motor fuels, the synthesis products of different boiling ranges are separated from the reaction water and the products dissolved therein, and processed. These products which are processed include a primary gasoline fraction, a Diesel oil fraction and still higher boiling hydrocarbons. The higher boiling hydrocarbon mixtures, i.e. the "reactor paraffins" are subjected to a thermal or catalytic cracking. Since the products of the

catalytic carbon monoxide hydrogenation predominantly consist of straight-chain and saturated hydrocarbons, the cracking of these products as contrasted with the cracking of natural petroleum products may be effected without the formation of coke, hydrogen-poor fuel oils, aromatic hydrocarbons, resins and cracking residues.

The primary gasolines and cracked gasolines obtained are subjected to a hot refining after treatment with bleaching earths or other aluminum silicates at elevated temperatures as, for example, at about 450°C. This results in an isomerization and a displacement of the unsaturated double linkages from the terminal to the middle position in the molecule.

One object of this invention is a process for the operation of a thermal cracking reactor, a fractionating column and a hot refining unit for the processing of synthesis products from carbon monoxide hydrogenation into gasoline and Diesel oil which is extremely favorable from an operational point of view with respect to heat economy. This and still further objects will become apparent from the following description read in conjunction with the drawing in which

Fig. 1 is a flow sheet showing an embodiment of a plant set-up for effecting the process in accordance with the invention, and

Fig. 2 is a flow sheet of a further embodiment of a plant set-up operating in accordance with the invention.

It has now been found that the synthesis products obtained by catalytic carbon monoxide hydrogenation may be cracked with practically no residue and it is possible to effect a combination of the thermal cracking of the high boiling hydrocarbons, of the fractionation of the total products and of the hot refining of the hydrocarbons boiling in the gasoline range. The combination has been found to be extremely favorable from

an economic and operational standpoint and with respect to the heat technology. This combination will herein after be referred to as "Thermo forming".

5 The products treated, in accordance with the invention, are the total primary products from carbon monoxide hydro-  
genation which may be liquefied at normal pressure exclusive of the reaction water and products dissolved therein. These products will be referred to herein after as the primary synthesis products. The products in the boiling range of about  
10 the reactor paraffins will be referred to as the higher boiling primary synthesis products while the remainder of the products, i.e. the heat exchanger condensate, the cold condensate and the low temperature condensate, will be referred to as the lower boiling primary synthesis products.

15 In accordance with the invention, the treatment of the primary synthesis products for the processing into gasoline and Diesel oil with fractionation thermal cracking of the higher boiling constituents and hot refining of the gasoline range boiling hydrocarbons is so effected that the higher boiling  
20 primary synthesis products are passed through a cracking reactor and the cracked products are passed to a fractionating column. The lower boiling primary synthesis products including the heat exchanger condensate, the cold condensate and the low temperature condensate are also passed to this fractionating column.  
25 In the fractionating column, the hydrocarbons in the gasoline and Diesel oil boiling range are separated. The gasoline range boiling hydrocarbons are passed in indirect heat exchange contact with the hot cracked product coming from the cracking reactor and thereafter through a hot refining unit. The Diesel  
30 oil is recovered from the fractionating column and gasoline is recovered from the hot refining unit. The sensible heat of the gasoline coming from the hot refining unit is preferably also

utilized in accordance with the invention. This may be effected, for example, by passing the same in indirect heat exchange contact with a portion of the lower boiling synthesis products being passed through the fractionating column or by passing the same in indirect heat exchange contact with the gasoline boiling range hydrocarbons being passed from the fractionating column to the hot refining unit prior to the indirect heat exchange contact with the cracked product from the cracking reactor. The fractionation of the primary products and the cracked products is effected in a common fractionation unit.

The operation of the "Thermoforming" process is illustrated in the flow sheets.

"Reactor paraffin" is sucked from tank 1 and heated to 450-500°C. in tubular furnace cracking reactor 2 while maintaining the pressure at such a level that the reactor paraffin will not evaporate. After adequate heating, the hydrocarbons, while being released from pressure, are passed into a separator 3 where a separation of vaporous and liquid constituents takes place. Water vapor which has been heated in tubular furnace 2 to about 500°C. is simultaneously passed through line 4 into separator 3.

Tank 5 contains the "heat exchanger condensate". It is pre-heated in heat exchanger 6 and at first passed into column 13 where any low boiling constituents are removed. From the bottom of column 13, the high boiling constituents of the "heat exchanger condensate" pass at first into a separate tubular coil positioned in the tubular cracking reactor 2 where they are heated to 500-520°C. Then under a pressure of 3-10 kg./sq.cm., the high boiling constituents pass into the vapor-liquid separator 3 mentioned above.

From separator 3, the still liquid product, together with the reactor paraffin flowing in from tank 1, is returned

into the cycle to be heated and cracked again. The products escaping from separator 3 in the vaporous form, together with the injected water vapor, pass through the cracking zone of the tubular furnace 2. Following this, they pass through a cooler and heat exchanger 7. The constituents which, after cooling, are still in the gaseous state are passed to a fractionating column 13. The hydrocarbons liquefied in cooler 7 are recycled to the cracking furnace 2. A small part of the liquid products is branched off and separated from polymerized portions in a small distilling column 8 operated with water vapor. The polymerisates are withdrawn as the bottom product while the gaseous overhead products are passed to the fractionating column 13.

The "cold condensate" contained in tank 9 is passed through a heat exchanger 10 and into the fractionating column 13. The condensate contained in tank 11 of the oil scrubbing unit, low-temperature treating unit or active carbon treating unit (low temperature condensate) is likewise passed, via heat exchanger 12, to the column 13. At the top of column 13, gasoline and cracked gases are withdrawn. In separator 14, the gasoline condensed in heat exchanger 12 is separated from the gaseous constituents. This gasoline, except for the part returned as reflux to the top of the column, passes to heat exchanger 7 where it is evaporated and heated to the reaction temperature (about 450°C.) of the bleaching earth treatment (hot refining).

In cases where the boiling range of the primary products to be processed is shifted to a larger extent into the area of the low boiling hydrocarbons and the portion of hydrocarbons to be cracked is consequently smaller, the gasoline coming from separator 14, prior to being heated in heat exchanger 7 is evaporated and pre-heated in heat exchanger 6. In these cases,

the heat exchanger condensate coming from storage container 5 is preheated in another suitable manner.

The gasoline vapors, adequately heated in exchanger 7 or in exchanger 6 and 7, pass through two or more alternately operated reactors 15 in which the isomerization of the hydrocarbons is effected on bleaching earths or other suitable catalysts. The sensible heat of the vapors flowing off from the isomerization unit is transferred in heat exchanger 6 to the "heat exchanger condensate" to be processed and coming from storage tank 5 or, as mentioned above, to the gasoline to be evaporated and coming from separator 14. Thereafter, the gasoline hydrocarbons treated with bleaching earth or other catalysts are passed to a rerun distillation unit to remove higher boiling constituents which may form in a small quantity during the isomerization.

The cracked gases obtained by distillation in fractionating column 13 and separated in separator 14 are passed to a storage container 16 and, from thence, are sucked by a compressor 17 and compressed for the purpose of recovering  $C_3C_4$  hydrocarbons.

The hydrocarbons boiling in the Diesel oil range are withdrawn from fractionating column 13 via a stripper 18. The sensible heat of these hydrocarbons is used, in heat exchanger 10, for heating the "cold condensate" coming from tank 9. Thereafter, the Diesel oil fraction is passed into a storage container 19.

The residues collecting at the bottom of column 13, as mentioned above, are returned to the cracking furnace 2.

The flow diagram shown in Fig. 2 illustrates a modified embodiment of the "Thermoforming" process.

Deviating from the operation method illustrated in Fig. 1, the gases leaving the cracking furnace 2, prior to passing

through the heat exchanger 7, are passed into a chamber 8a where they are precooled (chilled) with injected cold oil. For this purpose, use is made of the "heat exchanger condensate" contained in storage tank 5 which previously flows through heat exchanger 6. In chamber 8a, due to the oil injection, liquid and solid constituents separate and are further processed in the steam-operated distilling column 8 just as in the embodiment of the process illustrated in Fig. 1. The gases flowing off from column 8 are combined with the cracking gases flowing off from container 8a.

A modification of the process of the invention which is independent of the type of polymerisate separation in container 8 and concerns the performance of the hot refining is also illustrated in Fig. 2.

In the "Thermoforming" process, the heat requirements of the reaction, as is known, are met by the sensible heat of the entering gasoline vapors. During the passage through the apparatus, the vapors correspondingly cool down. It is preferable for some products if the gases are not allowed to cool down to such a low level during hot refining and if the reaction is effected in two stages in order that the gasoline vapors can be heated between the stages.

The effluent gases from the first stage of the hot refining unit 15 are heated by hot cracked gases in a heat exchanger 7a. The products leaving the second stage of the bleaching earth treating unit 15 transfer a part of their heat in heat exchanger 6a to the gasoline flowing off from separator 14 before this gasoline is further heated in heat exchanger 7. The heat content remaining thereafter of the products treated with bleaching earth, just as in the embodiment illustrated in Fig. 1, is transferred to the "heat exchanger condensate" coming from storage tank 5.



For the regeneration of the bleaching earths used for the hot refining step, an additional reactor is required which in Fig. 2 is designated by the numeral 15c. The reactors 15a to 15c operate in the conventional manner in a three-unit cycle. The reactor 15c, depending on the operational circumstances, may either cooperate with reactor 15a or with reactor 15b.

The process of the invention for processing carbon monoxide hydrogenation products into gasoline and Diesel fuels results in a considerable saving in investment and operation cost as compared with the conventional mode of operation. It is now possible to simultaneously meet the heat requirements for the fractionation of the primary products and for performing the hot refining of the hydrocarbons boiling in the gasoline range (isomerization) with the same amount of heat which was hitherto alone necessary for the thermal cracking of the high boiling constituents. The savings of equipment include two tubular furnaces and a fractionating unit for the primary products. The operation cost of the plant is likewise reduced to a corresponding extent.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. Process for the operation of a thermal cracking reactor, a fractionating column and a hot refining unit for the processing of synthesis products from catalytic carbon monoxide hydrogenation into gasoline and Diesel oil which comprises passing the higher boiling primary synthesis products through the cracking reactor, passing the cracked product from the cracking reactor to the fractionating column, passing the lower boiling primary synthesis products to the fractionating column, separating gasoline and Diesel oil range hydrocarbons in the fractionating column, passing the gasoline range hydrocarbons in indirect heat exchange contact with the cracked product coming from the cracking reactor and there after through the hot refining unit and recovering gasoline from the hot refining unit and Diesel oil from the fractionating column.

2. Process according to Claim 1 in which a portion of the lower boiling primary synthesis products is passed in indirect heat exchange contact with the gasoline from the hot refining unit prior to being passed to the fractionating column.

3. Process according to Claim 2 in which the heat exchanger condensate portion of the lower boiling primary synthesis products is passed in indirect heat exchange with the gasoline from the hot refining unit prior to being passed to the fractionating column.

4. Process according to Claim 1 in which the gasoline range hydrocarbons are passed in indirect heat exchange contact with the gasoline from the hot refining unit prior to being passed in indirect heat exchange with the cracked product from the cracking reactor.

5. Process according to Claim 1 which includes partially pre-cooling the effluent gases from the cracking reactor by

injecting a portion of the heat exchanger condensate portion of the lower boiling primary synthesis products.

6 Process according to Claim 1 in which the hot refining unit has at least two stages and in which the gasoline range hydrocarbons being passed from the first stage ~~to~~<sup>to</sup> the second stage are passed in indirect heat exchange contact with a portion of the cracked product from the cracking reactor.

7 Process according to Claim 1 in which the heat exchanger condensate portion of the lower boiling primary synthesis products is passed in indirect heat exchange with the gasoline from the hot refining unit prior to being passed to the fractionating column, the cold condensate portion of the primary synthesis product is passed in indirect heat exchange contact with the Diesel oil from the fractionating column prior to being passed through the fractionating column, and the low temperature condensate portion of the lower boiling primary synthesis products is passed in indirect heat exchange contact with the overhead product from the fractionating column prior to being passed to the fractionating column.

8 Process according to Claim 1 in which the heat exchanger condensate portion in the lower boiling primary synthesis products is passed in indirect heat exchange contact with the gasoline from the hot refining unit, thereafter a portion passed to the fractionating column and the remainder injected into the cracked product from the cracking reactor for the partial pre-cooling thereof, a portion of the cracked product after said injecting being passed in indirect heat exchange contact with the gasoline range hydrocarbon passing from a first to a second stage in the hot refining unit and another portion being passed in indirect heat exchange contact with the gasoline range hydrocarbon being passed to the hot refining unit, the cold condensate portion of the low boiling primary synthesis products being passed in indirect heat

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exchange contact with the Diesel oil from the fractionating column prior to being passed to the fractionating column and the low temperature condensate portion of the low boiling primary synthesis products being passed in indirect heat exchange contact with the overhead product from the fractionating column prior to being passed to the fractionating column.

9 Process according to Claim 8 in which the gasoline range hydrocarbons are passed in indirect heat exchange contact with the gasoline from the hot refining unit prior to being passed in indirect heat exchange contact with a portion of the cracked product from the cracking reactor, said indirect heat exchange contact between the gasoline from the hot refining unit and the gasoline range hydrocarbon being effected prior to the indirect heat exchange contact between the gasoline from the hot refining unit and the heat exchanger condensate portion of the lower boiling primary synthesis product.

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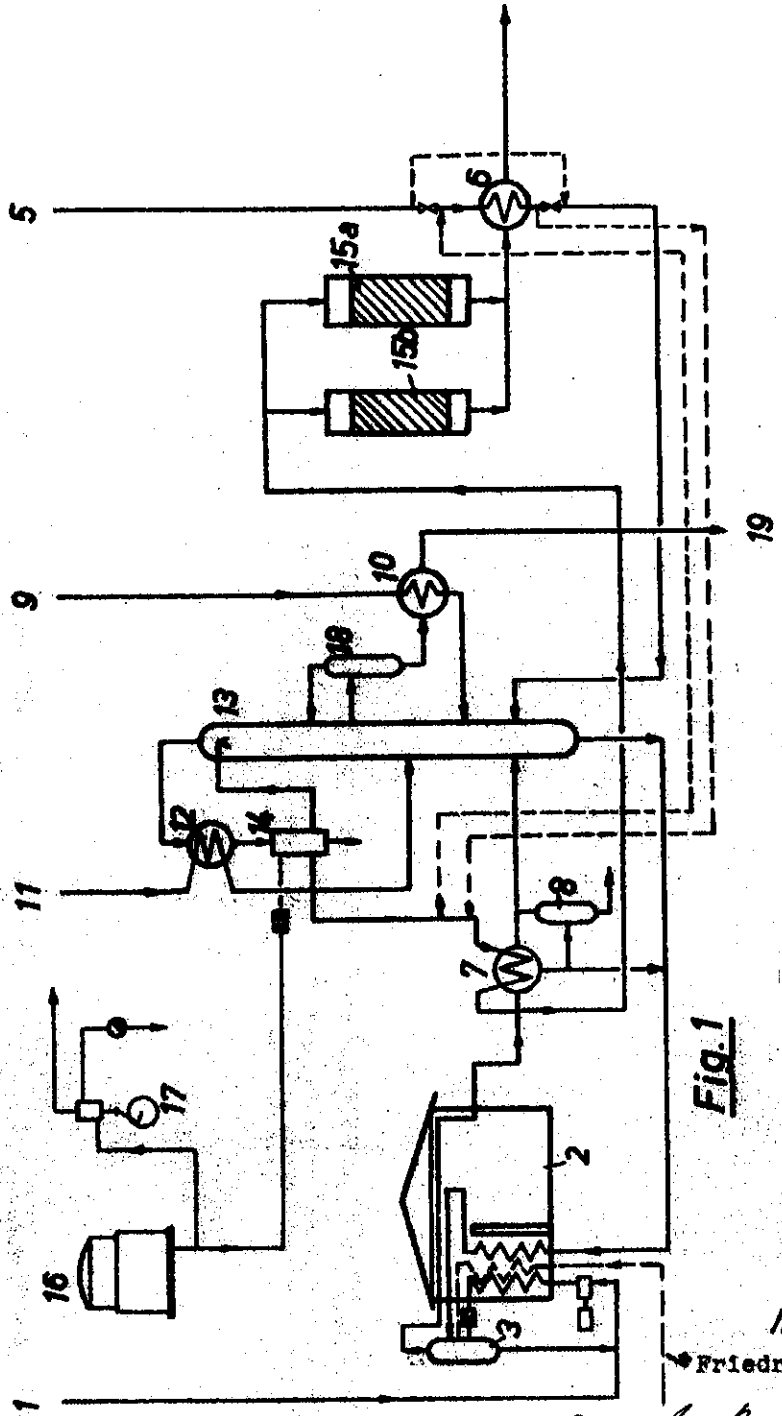
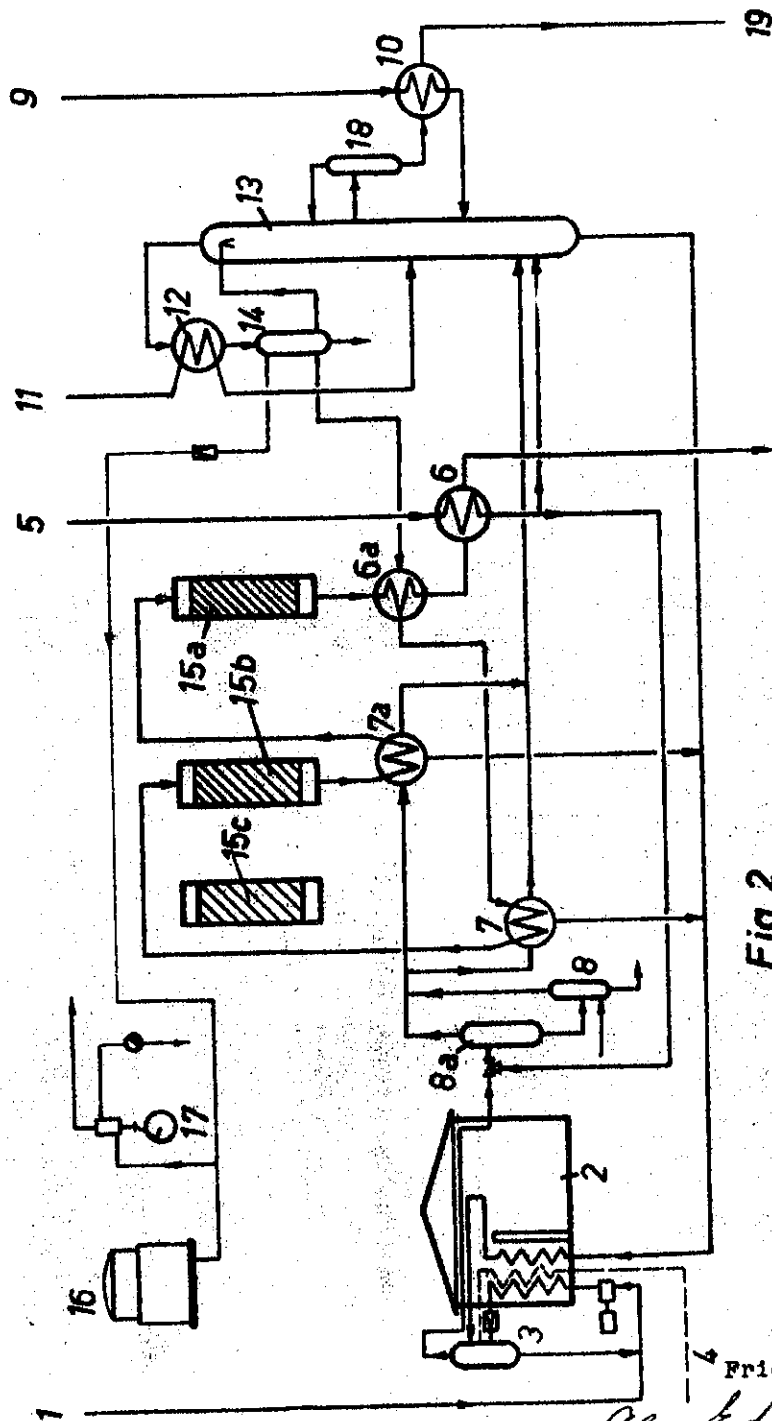


Fig. 1

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**Fig. 2**

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