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PATENT SPECIFICATION

Convention Date (Germany): July 30, 1937.

517,002

Application Date (in United Kingdom): July 27, 1938. No. 22394/38.

Complete Specification Accepted: Jan. 17, 1940.

3699

COMPLETE SPECIFICATION

Process for Producing Solid Paraffin from Carbon Monoxide and Hydrogen

We, STUDIEN- UND VERWERTUNGS-GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of 2, Kaiser-Wilhelm-Platz, Mülheim-Ruhr, Germany, a Body Corporate organised and existing under the Laws of the German State, 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:—

It is known that when benzine synthesis is carried out under atmospheric pressure and using highly active catalysts that contain metals of the eighth group of the periodic system, aliphatic hydrocarbons having a wide range of boiling points—amongst them paraffin wax—are produced from gases containing carbon monoxide and hydrogen. The quantity of paraffin wax varies, according to the process conditions, between 4 and 10%, and is thus quantitatively far less than the other reaction products. Thus by far the largest part of the reaction products passes out from the reaction chamber in the form of vapours or gases. The relatively small quantities of paraffin wax remaining on the catalyst may be removed by extraction or other known means after the expiration of the reaction period, that is to say, after several weeks or months.

It was found, in connection with benzine synthesis, that it was best that for every kg. of cobalt—or (which amounts to practically the same thing) for every 10 litres-capacity of contact chamber—about 1 cubic metre of a mixture of carbon monoxide and hydrogen should be subjected to conversion per hour. With such a relation between the volume of gas to be converted and the contact mass or contact chamber capacity about 100 gms. per hour of reaction products can in benzine synthesis be obtained at the commencement of a working period, and after a period of 6 to 8 weeks 80 gms. per hour of reaction products can be obtained per cubic metre of the carbon monoxide and hydrogen mixture. If only 50%, or even only 10%, of the volume hereinbefore mentioned of gas to be converted is passed per hour through the contact chamber, there is a slight increase in yield of reaction products obtainable per cubic metre of carbon monoxide and hydrogen, but this method of working is not economical since the volumes of initial gas passed through the contact chamber are too small. The nature of the reaction products remains approximately the same at atmospheric pressure under reduced velocity of the gases or with longer duration of the conversion period. The reaction products consist almost exclusively of oil, benzine and gasol or gaseous hydrocarbons with 2 or more carbon atoms in the molecule.

Furthermore, carbon monoxide and hydrogen have previously been caused to react with cobalt catalysts under increased pressure, for example, at 5 or 80 atmospheres. In connection with these reactions with regard to the quantity of gas to be converted, it was necessary to bear in mind that in raising the pressure, for example, to five times as much it is possible to pass through the apparatus five times the volume of gas (measured at atmospheric pressure) per unit of time. In this connection a lead was given from analogous conditions in other processes. Therefore in all previous work either the process was carried out under widely varying pressures and with about the same volumetric throughput (measured under the prevailing pressure) of the gases in the reaction chamber, or closed vessels were employed in which the gases introduced were forced to remain, or the influence of the contact period of the gases in the contact chamber was not taken into account.

Under increased pressure the proportion of paraffin wax in the product obtained increases.

According to the invention, a process has been found for the production of paraffin wax from gases containing carbon monoxide and hydrogen using catalysts of cobalt, or a mixed catalyst containing cobalt at temperatures lying below 250° Centigrade and under pressures of at least 3 atmospheres according to which the volumetric throughput (measured under the prevailing pressure) of the gases is determined by ascertaining the optimum volumetric throughput at atmospheric pressure, i.e. the volumetric throughput giving the maximum yield of all the hydrocarbons containing at least 2 carbon atoms in the molecule and decreasing this volumetric throughput approximately proportionately to the increase in the working pressure, that is, to say, when the pressure is raised the quantity of gas by weight passed through the contact chamber per hour is the same as that which gives the optimum yield at atmospheric pressure. Thus, in order to obtain optimum yields of solid hydrocarbons it is necessary to work at 5 atmospheres, with a volumetric throughput, measured at 5 atmospheres, which is five times smaller than that ascertained at atmospheric pressure, and at 20 atmospheres with a volumetric throughput about twenty times smaller than that maintained at atmospheric pressure. If on the other hand the throughput in volume selected for 20 atmospheres pressure and measured at 20 atmospheres is taken twice as large namely only 10 times smaller than that ascertained for atmospheric pressure, the yield of the solid hydrocarbons drops by from 30—50% although the throughput by weight is twice as large as when operating at a working pressure of 5 atmospheres. A decrease in the throughput below that which results in the optimum yield of solid hydrocarbons the pressure remaining unchanged, is found to offer no advantage, as the rate of increase in the yield decreases to an extent that cannot be justified on economic grounds. When working with gases that do not flow through the reaction chamber the results are definitely not so good, as the products are then exposed for too long a period to the action of the contact mass. Very favourable results in regard to the yield obtainable per cubic metre of initial gas, and also with respect to the life of the contact mass, are secured if the reaction be carried out at a pressure of from about 5 to 20 atmospheres while maintaining the inverse relation between the volumetric throughput of the gases and the pressure. It has furthermore been found an advantage so to select the pressure of the gases that it is equal to the pressure of saturated steam at the synthesis temperature. The range of pressure of from 2 to 50 atmospheres is that which is preferred. Higher pressures may be used, but they are often accompanied by increased cost without a resultant advantage to the efficiency of the process.

If it is desired to remove the reaction heat by water cooling, it is advisable to operate with the same working pressure in the reaction chamber as in the water outside the reaction chamber, as then the contact chambers cannot be stressed by pressure either from the outside or from the inside, and can thus be made of an inexpensive material. The use of cobalt catalyst renders it necessary that the process should be carried out at temperatures lying below 250° C.

EXAMPLE.

A contact mass produced by precipitation and consisting of cobalt, thoria and kieselguhr is first tested for activity under atmospheric pressure with a gas consisting of one part of carbon monoxide and two parts of hydrogen by volume. It is found that at, for example 190° C. a throughput of 100 litres of gases per litre of contact chamber per hour gave a maximum yield of hydrocarbons containing at least 2 carbon atoms per molecule which consisted for the greater part of liquid hydrocarbons. The contraction which amounted to 80% was also a maximum. An increase in the rate of gas throughput caused the formation of the undesired gaseous hydrocarbons, while a raising or lowering of the reaction temperature produced an incomplete conversion of carbon monoxide. If it is desired to produce not liquid hydrocarbons but large quantities of paraffin wax, the pressure must be increased and at the same time the volumetric throughput (measured under the prevailing pressure) of the gases must be decreased merely proportionately thereto. Since it is necessary during a long working period to raise the working temperature slowly, it is desirable to increase at the same time the pressure to obtain a high yield of paraffin wax. It is advantageous to work at, for example 180° C. at a pressure of 10 atmospheres and a volumetric throughput (measured at 10 atmospheres) which is ten times smaller than that for working at atmospheric pressure, and, on raising the temperature to 200° C. at a pressure of 15 atmospheres and with a volumetric throughput (measured at 15 atmospheres) fifteen times as small as that employed for atmospheric pressure. The highest yields of all hydrocarbons including optimum yields of paraffin wax, namely from about 150 to 160 gm. per cubic metre of gas (calculated with respect to a mixture consisting of $1CO:2H_2$), is obtained at a pressure of from 5 to 20 atmospheres and with a volumetric throughput (measured under the prevailing pressures) 5 to 20 times smaller than that required when operating at atmospheric pressure. After one year's work a quantity of approximately 100 gm. is still obtained with the same contact mass without regeneration.

The catalyst preferably rests on a permeable support, for example, on sieves, so that paraffin wax formed during the reaction can trickle at the reaction temperature in molten condition from the catalyst. The hydrocarbons of low boiling point formed beside the paraffin wax are obtained from the resulting gases by condensation or adsorption. The paraffin wax adsorbed by the catalyst may, if desired, also be obtained by extraction with a solvent for paraffin wax, for example, by extraction with benzine.

If, with a view to simplifying the apparatus it is desired to work under the same pressure in the contact chamber as in the cooling chamber, such yields are obtained at temperatures of from 175 to 205° C. and under corresponding pressures of 8 to 17 atmospheres with a volumetric throughput of the gases that is numerically from eight to seventeen times as small as for the optimum throughput at atmospheric pressure.

Up to 60% of the total reaction products boil at over 300° C. and consist of a perfectly white odourless paraffin that is solid at room temperature and that at about 100° C. melts to give a perfectly clear liquid. The remaining 40% of the reaction products consist of oil, benzine and gasol. The paraffin wax thus obtained may be employed as such or may form the basis from which to produce fatty acids. It may also be used for producing olefines and anti-knock benzine by cracking, as the large yield provided by the process compensates for the losses during cracking.

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 producing paraffin, solid at room temperature, that is to say, paraffin wax, from gases containing carbon monoxide and hydrogen, using catalysts of cobalt or a mixed catalyst containing cobalt, at temperatures lying below 250° C. and under pressures of at least 2 atmospheres, in which the volumetric throughput (measured under the prevailing pressure) of the gases is determined by ascertaining the optimum volumetric throughput, i.e. the volumetric throughput giving the maximum yield of all hydrocarbons containing at least 2 carbon atoms per molecule at atmospheric pressure and decreasing this volumetric throughput approximately proportionately to the increase in the working pressure, that is to say, when the pressure is raised the quantity of gas by weight passed through the contact chamber per hour is the same as that which gives the optimum yield at atmospheric pressure.

2. A process according to claim 1 which is carried out under a pressure of from 2—50 atmospheres.

3. A process according to claim 1, which is carried out under a pressure of from 5 to 20 atmospheres.

Dated this 27th day of July, 1938.

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Chartered Patent Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1940.