PATENT SPECIFICATION

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536,169

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PROVISIONAL SPECIFICATION

Improvements in the Production of Hydrocarbons by the Catalytic Conversion of Carbon Monoxide

I, HAROLD EDWIN POTTS, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention which has been communicated to me by N. V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company), of 20, Wassenaarscheweg, The Hague, Holland, a Dutch Company, to be as follows:—

In the catalytic conversion of carbon monoxide with hydrogen for the production of hydrocarbons with more than one carbon atom in the molecule the reaction temperature has to be maintained within narrow limits.

It has already been proposed for a rapid removal of the heat generated in strongly exothermic conversion to surround the reaction space with liquids undergoing vaporisation, in particular water undergoing vaporisation. The vapour is condensed and returned to the cooling space, in a closed cooling system. Alternatively, the vapour formed is employed for heating purposes or for generating power. The amount of cooling liquid vaporised must according to the second alternative be replaced by fresh liquid and if impure cooling liquid is used, difficulties may be encountered due to the formation of deposits, such as boiler-scale.

It has already been proposed when using several reaction systems to collect the vapour formed from the cooling liquid in one common vessel. In this case the drawback is encountered that the temperature regulation of the various reaction systems becomes less flexible since for all reaction systems the cooling liquid has the same temperature, namely that of the common vessel in which the vapour, for example, steam is collected.

My foreign correspondents have now found that in the catalytic conversion of carbon monoxide with hydrogen for the production of hydrocarbons containing more than one carbon atom in the molecule in a plurality of reaction systems the said drawbacks do not occur when carrying out the removal of the heat generated by means of a cooling liquid, if the cooling liquid for each reaction system is contained in a separate closed cooling system, in each of which the cooling liquid is vaporised in a cooling space by indirect heat exchange with the contents of that reaction system to which the cooling system belongs and the vapours of the cooling liquid are condensed and returned to the cooling space, and if the condensation of the vapours of separate cooling systems belonging to two or more reaction systems is effected by indirect heat exchange with a liquid undergoing vaporisation in a common secondary vaporiser.

In Figure 1 of the accompanying drawing, an apparatus for use in the process in accordance with the present invention is illustrated diagrammatically, whereas in Figure 2 a reaction system with the closed cooling system belonging to it is illustrated in greater detail.

Referring to Figure 1, to each reaction system *a*, a^{1}, a^{11}, a^{111} belongs a separate closed cooling system 1, 2, 3 and 4 respectively. The condensing coils *d*, d^{1}, d^{11} and d^{111} for said closed cooling systems are contained in a common secondary vaporiser *e* for the transmission of heat from the vapours of the cooling liquid to liquid undergoing vaporisation in the said secondary vaporiser. The cooling systems are respectively provided with valves *g*, g^{1}, g^{11} and g^{111} for regulating the vapour pressure therein as described in greater detail below.

Since the reaction systems or single reaction spaces therein may be maintained at considerably different temperatures and the evolution of heat in the reaction spaces may change in the course of a period of operation, it is advisable, as the heat-exchange surfaces of the condensing coils *d*, d^{1}, d^{11} and d^{111} are approximately of similar size and invariable, to adjust the transmission of heat of the coils to the development of heat in the reaction space by regulation of the vapour pressure and thereby of the temperature of the vapour in the condensing coils.

This can be attained as has been shown

[*Price* 1/-]

Price 4s 6d.

in Figure 2, by regulating valve *g*, constructed in the vapour line *c* which is operated by hand or automatically, and which throttles the flow of vapour to the condensing coil *d*, in case the vapour pressure in separator *b*, in which vapours separate from liquid, falls below a predetermined value. By the drop of the vapour pressure behind the regulating valve in the vapour line *c* and in the condensing coil *d* also the temperature of the vapour decreases at these places as also the amount of heat transmitted to the liquid undergoing vaporisation in the secondary vaporiser *e*. By the lowering of the vapour pressure in line *c* and condensing coil *d* liquid is pressed upwards in the line *f* by the higher pressure in the separator *b*. In case the difference in level between coil *d* and separator *b* is not sufficient to allow of the pressure of the column of liquid rising in *f* to compensate the reduction in vapour pressure in line *c* and condenser *d* due to the throttling of the vapour by valve *g* the column of liquid in *f* is sucked up to condenser *d* so that the transmission of heat in the vaporiser *e* decreases further until equilibrium between evolution of heat in *a* and the transmission of heat of condenser *d* in *e* is attained.

While water may be employed as a cooling liquid in the closed cooling system the described process is particularly advantageous in those cases where the employment of another liquid than water as cooling liquid is preferable. This will be the case if the conversion temperature is so high that apparatus which stand the vapour pressure then prevailing are very expensive. Then it is more advantageous to use as cooling liquid in the closed system a liquid with a low vapour pressure, for example, di-phenyl oxide, whereby the vapour of di-phenyl oxide is used for generating steam in the secondary vaporiser *e* which can be constructed at considerably less expense than the total apparatus in a manner so that it stands a high vapour pressure.

The construction of the reaction spaces can be chosen at will, in so far as these are suitable for cooling with a liquid undergoing vaporisation. Several reaction spaces may be combined in one reaction system cooled by a single closed cooling system. *Inter alia* a number of reaction tubes may be contained in a single cooling space, or the cooling liquid for a single reaction space may be contained in a large number of tubes all connected with one cooling system.

The conversion temperatures in general lie between 150° and 380° Centigrade. The process may be worked at ordinary or increased pressure, for example, between 5 and 30 atmospheres or also at higher pressures such as 100 atmospheres and more.

The process makes possible a very simple construction of the cooling devices for the reaction spaces. A further great advantage consists in the fact that these cooling spaces which are only very difficultly accessible, remain protected from any collection of boiler scale and sludge, since always the same cooling liquid flows in a circular course. The process renders it further possible by the application of liquids other than water to maintain in the cooling spaces temperatures which are substantially above the temperature range of boiling water at ordinary and moderately elevated pressures. Finally, owing to the employment of a number of separate cooling systems and a secondary common vaporiser a great flexibility of temperature regulation in a plant operating with a considerable number of reaction systems is attained.

Dated this 29th day of September, 1939.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in the Production of Hydrocarbons by the Catalytic Conversion of Carbon Monoxide

I, Harold Edwin Potts, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention which has been communicated to me by N. V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company), of 20, Wassenaarscheweg, The Hague, Holland, a Dutch Company, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In the catalytic conversion of carbon monoxide with hydrogen for the production of hydrocarbons with more than one carbon atom in the molecule the reaction temperature has to be maintained within narrow limits.

It has already been proposed for a rapid removal of the heat generated for example in strongly exothermic conversion reactions to surround the reaction space with liquids undergoing vaporization, in particular water undergoing vaporization. The vapour formed may be employed for heating purposes or for generating power. The amount of cooling liquid vaporised must be replaced by fresh liquid and if impure cooling liquid is used, difficulties may be encountered due to the formation of deposits, such as boiler-scale. The vapour may be therefore condensed and returned to the cooling space in a closed cooling system.

It has already been proposed when using several reaction systems to collect the vapour formed from the cooling liquid in one common vessel. In this case the drawback is encountered that the temperature regulation of the various reaction systems becomes less flexible since for all reaction systems the cooling liquid has the same temperature, namely that of the common vessel in which the vapour, for example, steam is collected.

My foreign correspondents have now found that in the catalytic conversion of carbon monoxide with hydrogen for the production of hydrocarbons containing more than one carbon atom in the molecule in a plurality of reaction vessels (arranged in series or in parallel or independently of each other) with the removal of the heat generated in the reaction vessels by means of a cooling liquid, the above disadvantages can be avoided if the cooling liquid for each reaction system is contained in a separate closed cooling system, in each of which the cooling liquid is vaporised in a cooling space by indirect heat exchange with the contents of that reaction system to which the cooling system belongs and the vapours of the cooling liquid are condensed and returned to the cooling space, and if the condensation of the vapours of separate cooling systems belonging to two or more reaction systems is effected by indirect heat exchange with a liquid undergoing vaporisation in a common secondary vaporiser.

In Figure 1 of the drawing accompanying the Provisional Specification an apparatus for use in the process in accordance with the present invention is illustrated diagrammatically, whereas in Figure 2 a reaction system with the closed cooling system belonging to it is illustrated in greater detail. Referring to Figure 1, to each reaction system a, a^1, a^{11}, a^{111} belongs a separate closed cooling system 1, 2, 3 and 4 respectively. The condensing coils d, d^1, d^{11} and d^{111} for said closed cooling systems are contained in a common secondary vaporiser e for the transmission of heat from the vapours of the cooling liquid to liquid undergoing vaporisation in the said secondary vaporiser. The cooling systems are respectively provided with valves g, g^1, g^{11} and g^{111} for regulating the vapour pressure therein as described in greater detail below.

Since the reaction systems or single reaction spaces therein may be maintained at considerably different temperatures and the evolution of heat in the reaction spaces may change in the course of a period of operation, it is advisable, as the heat-exchange surfaces of the condensing coils d, d^1, d^{11} and d^{111} are approximately of similar size and invariable, to adjust the transmission of heat of the coils to the development of heat in the reaction space by regulation of the vapour pressure and thereby of the temperature of the vapour in the condensing coils.

This can be attained as has been shown in Figure 2, by regulating valve g, constructed in the vapour line c which is operated by hand or automatically, and which throttles the flow of vapour to the condensing coil d, in case the vapour pressure in separator b, in which vapours separate from liquid, falls below a predetermined value. By the drop of the vapour pressure behind the regulating valve in the vapour line c and in the condensing coil d also the temperature of the vapour decreases at these places as also the amount of heat transmitted to the liquid undergoing vaporisation in the secondary vaporiser e. By the lowering of the vapour pressure in line c and condensing coil d liquid is pressed upwards in the line f by the higher pressure in the separator b. In case the difference in level between coil d and separator b is not sufficient to allow of the pressure of the column of liquid rising in f to compensate the reduction in vapour pressure in line c and condenser d due to the throttling of the vapour by valve g the column of liquid in f is sucked up to condenser d so that the transmission of heat in the vaporiser e decreases further until equilibrium between evolution of heat in a and the transmission of heat of condenser d in e is attained.

While water may be employed as a cooling liquid in the closed cooling system the described process is particularly advantageous in those cases where the employment of another liquid than water as cooling liquid is preferable. This will be the case if the conversion temperature is so high that apparatus which stand the vapour pressure then prevailing are very expensive. Then it is more advantageous to use as cooling liquid in the closed system a liquid with a low vapour pressure, for example, di-phenyl oxide, whereby the vapour of di-phenyl oxide is used for generating steam in the secondary vaporiser *e* which can be constructed at considerably less expense than the total apparatus in a manner so that it stands a high vapour pressure.

The construction of the reaction spaces can be chosen at will, in so far as these are suitable for cooling with a liquid undergoing vaporisation. Several reaction spaces may be combined in one reaction system cooled by a single closed cooling system. *Inter alia* a number of reaction tubes may be contained in a single cooling space, or the cooling liquid for a single reaction space may be contained in a large number of tubes all connected with one cooling system.

The conversion temperatures in general lie between 150° and 380° Centigrade. The reaction may be carried out at ordinary or increased pressure, for example, between 5 and 30 atmospheres or also at higher pressures such as 100 atmospheres and more.

The process makes possible a very simple construction of the cooling devices for the reaction spaces. A further great advantage consists in the fact that these cooling spaces which are only very difficultly accessible, remain protected from any collection of boiler scale and sludge, since always the same cooling liquid flows in a circular course. The process renders it further possible by the application of liquids other than water to maintain in the cooling spaces temperatures which are substantially above the temperature range of boiling water at ordinary and moderately elevated pressures. Finally, owing to the employment of a number of separate cooling systems and a secondary common vaporiser a great flexibility of temperature regulation in a plant operating with a considerable number of reaction systems is attained.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A method of cooling a plurality of reaction vessels by means of cooling liquids in a process for the catalytic conversion of carbon monoxide into hydrocarbons containing more than one carbon atom in the molecule by reaction with hydrogen wherein the cooling liquid for each reaction system is contained in a separate closed cooling system in each of which the coolng liquid is vaporized in a cooling space by indirect heat exchange with the contents of that reaction system to which the cooling system belongs, and the vapours of the cooling liquid are condensed and returned to the cooling space, the condensation of the vapours of separate cooling systems belonging to two or more reaction systems being effected by indirect heat exchange with a liquid undergoing vaporization in a common secondary vaporizing system.

2. In the method as claimed in Claim 1, regulating temperature in each of the reaction systems by adjusting the heat given by the condensing cooling liquid in the secondary vaporizer to the development of heat in the reaction space by regulation of the vapour pressure of the cooling liquid at the place where it is condensed.

3. A method as claimed in Claims 1 and 2 in which a high boiling liquid is provided in each cooling system and water in the secondary vaporizing system.

4. An apparatus for carrying out the method of Claim 1 comprising a number of reaction vessels, coolers arranged in said reaction vessels containing cooling liquid, condensing coils connected to said coolers, and a common secondary vaporizer, containing said condensing coils.

5. An apparatus as claimed in Claim 1 in which a throttle valve is provided in each cooling system before the condensing coil.

6. An apparatus as claimed in Claim 4 or 5 comprising also separators for liquids and vapours connected to said condensing coils and connections for returning condensed liquid from the condensing coils to the cooling liquid in the coolers.

7. A process for the production of hydrocarbons containing more than one carbon atom in the molecule by catalytic conversion of carbon monoxide with hydrogen as particularly described.

8. An apparatus for the manufacture of hydrocarbons containing more than one carbon atom in the molecule by catalytic conversion of carbon monoxide with hydrogen as particularly described with reference to the accompanying drawings.

Dated this 18th day of September, 1940.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

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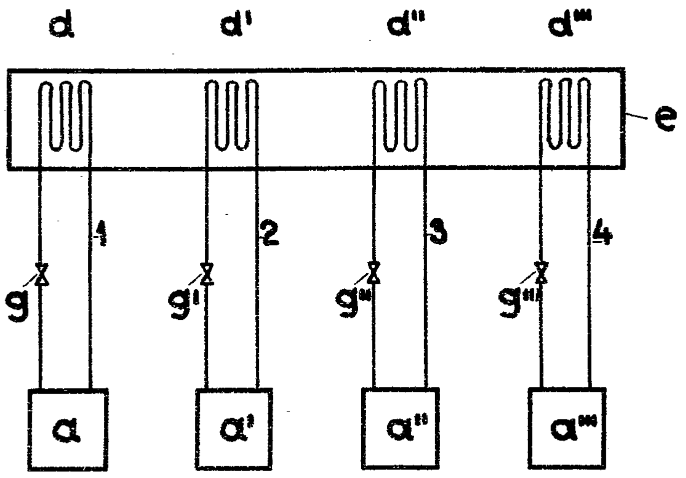
536,169 PROVISIONAL SPECIFICATION

1 SHEET

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

FIG. 1



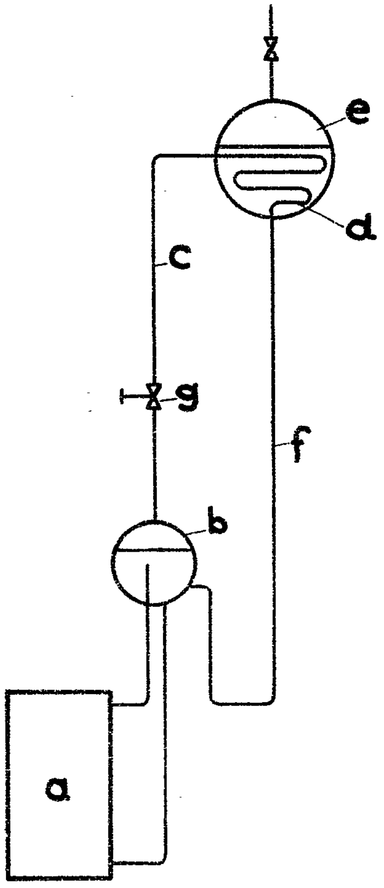


FIG. 2

Malby & Sons, Photo-Litn.