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The Processing of Products Resulting from the Conversion
of Carbon Monoxide with Hydrogen

In the catalytic conversion of carbon monoxide with hydrogen into multi-membered hydrocarbons at ordinary pressure and after separation of the higher boiling hydrocarbons, the low boiling hydrocarbons contained in the residual gas may be obtained by cooling and absorption with active charcoal. The latter is regenerated by treatment with steam, the absorbed hydrocarbons being thereby set free. They can then be again liquefied by condensation. The liquids then run into a separation vessel in which the lighter hydrocarbons collect in a layer at the top and the water flows out at the bottom; the top layer can be drawn off, as a rule, continuously. If the conversion of carbon monoxide and hydrogen be carried out at higher pressures, e.g. at intermediate pressures, the conversion products can be processed in the same manner. Here, as well as in the case of the ordinary pressure synthesis, not only solid but also liquid absorption agents can be used, such as wash oil, cuts of heavy gasoline et. al. for the purpose of removing the low-boiling components from the residual gas.

All words followed by * are words which are handwritten in the German text (Transl.)

If the carbon monoxide is converted with hydrogen in the presence of catalysts belonging to the iron group, or preferably iron, and at temperatures which are below the temperature at which with the same catalyst mainly hydrocarbons would be formed (as stated in Patents and (Appl. I. 70 503 IVd/12o dated 25 September 1941 and I. 73 384 IVd/12o dated 16 October 1942)), then the conversion will take a somewhat different course: products are obtained which have a substantial content of oxygenated organic compounds, especially alcohols; in most cases, they will amount to at least 20%, but as a rule there will be 30-40% of oxygen containing compounds, besides the higher hydrocarbons. In the processing of these products one finds that the water formed during the reaction also contains lower molecular weight oxygen containing organic compounds, mainly alcohols. This water is formed in substantial amounts also in those cases in which the oxygen of the carbon monoxide which has not been fixed in the form of these organic compounds, is given off in the form of carbon dioxide. Considering the great solubility of the alcohols and of the oxygenated compounds in water, it could be assumed that these compounds would be separated, by condensing the water, to such an extent that the residual gas, when subjected to active charcoal treatment, would contain them in amounts hardly worth mentioning. However, it was found that from the aqueous condensate obtained from the vapors which are set free during the regeneration of the adsorption and absorption agents (the two latter will henceforth be generally designated as sorption agents) considerable amounts of the lower alcohols can be recovered; thus,

the yield of valuable products can be greatly augmented. Considerable amounts of low boiling alcohols are obtained; their concentration can be, for example, 2g, 5g, or even more, per m³ of synthesis gas.

The processing and break down of the alcohol-containing water can be accomplished by well known methods, especially distillation. Here, the disadvantage is that one has to distill a larger amount of water. But it was found that during the steam treatment of the sorption agent the low boiling alcohols do not distill over in a uniform manner; rather, at the beginning one will obtain a condensate much richer in alcohols than at the end. Furthermore, the alcohol content of the condensate keeps decreasing continuously during the distillation. It will therefore be sufficient to subject to distillation only the first portions (say the first half, third or fourth) of the product obtained by the steam treatment; and the distillation can then be continued only for the period of time necessary for most of the alcohol content to distill over. The residues going into the waste water of the aqueous condensate then contain only a small amount of alcohols, say about 1% or less.

It was further discovered that the advantage of processing small batches of water can be combined with the prevention of any alcohol loss; this can be done as follows: the vapors set free in the later period of the regeneration of the sorptive agent contain but small amounts of alcohol; instead of trying to recover their alcohol content right away, one uses these vapors for the regeneration of a fresh batch of sorptive agent; only then does

one treat them for alcohol recovery. This can be done in different ways. Should there be several sorption vessels, the following method can be applied: during the steam treatment of the content of one of the vessels, the first, strongly alcoholic vapors are condensed; the steam which follows, and which is lean in alcohols, is then passed through another vessel which contains strongly loaded sorption agent; the flow must be regulated so that this alcohol-lean vapor will be the first to be condensed after having passed through this stage. However, one can also take the alcohol-lean steam and condense it; then, one reconverts it into steam by means of an indirectly heated secondary evaporator when a loaded sorptive agent is to be regenerated. Thereby, use of the non-condensed steam as well as of the re-evaporated water can be regularly alternated.

In the distillation of the alcohol-containing water, auxiliary boiling agents can be added; also, all the known devices designed for a proper and convenient distillation and separation of the water from the alcohols can be used, e.g. columns with inbuilt plates, floors or grooves; also separation columns packed with filling bodies, etc. The distillation may be made either at normal or at reduced pressure. The separation can also be carried out by other, very different methods such as for instance extraction e.g. with hydrocarbons such as gasolines, esters insoluble in water (e.g. butyl acetate), or ethers. Since, as has been already mentioned, water is formed in the course of the synthesis, which contains a considerable amount of alcohols, and since this water must also be worked up, it can be processed

together with the aqueous condensate obtained from the sorption agent.

As adsorption agent, active charcoal is the most suitable, however, also other solid adsorption agents can be used, such as bleaching earths, gels, and others.

Absorption agents are liquids with low vapor pressure, for instance wash oil such as is used in the benzene washing; or intermediate and heavy oils of natural occurrence or prepared synthetically; particularly also the oil formed in the synthesis which can, if necessary, be freed from alcohols before use. The washing is best carried out in countercurrent: the gas is passed, through an appropriate washing unit, from bottom towards top while at the same time the washing agent is made to trickle downwards. The latter can be regenerated by steam or by additional heating. The hot regenerated washing agent can be cooled by indirect heat exchange with washing agent to be regenerated and led in countercurrent; the latter then yields, after having been treated with steam, the last traces of absorbed product. The final cooling of the regenerated oil is accomplished by using cooling water; the oil can then again be used as washing agent.

One or more sorption agents can be used, e.g. several solid or several liquid ones; or also, liquid and solid sorption agents one after the other. Thus one can, for instance take the final synthesis gas and first free it, by means of an oil wash, from its components in the boiling range of the C₅-C₉ hydrocarbons; one can then follow up with an active charcoal treatment, which will free the gas from the components which boil in the C₃ to C₄ hydrocarbon range.

The sorption process may take place either at normal or at higher pressure, e.g. first at the synthesis pressure (about 10-25 atm.), with a liquid; then the pressure can be released and treatment with active charcoal follows; this removes all the residual low boiling compounds. The steam treatment of the sorption agent can also take place at either normal or increased pressure. Should increased pressure be applied, one can obtain very low boiling hydrocarbons, such as the C_3 and C_4 hydrocarbons, as well as the higher boiling components, directly in liquid form.

The process of sorption is best carried out at the lowest possible temperatures. Thus one can, for example, precool the gas to a greater or lesser extent; the same can be done with the liquid sorption agents if they are being used in the process. If one operates with solid sorption media, the gas can be cooled either before or between the various sorption stages. One can also, by means of inner cooling installations, cool the sorption agent itself in order to remove the heat given off during the sorption process and thus prevent an undesirable temperature increase. The cooling of the sorption agents can be done by any desired method, for instance by passing through of air, fresh synthesis gas, synthesis end gas, etc.

For the regeneration of the sorption agent, low pressure ~~steam of temperatures a little above 100° is generally sufficient.~~ However, one may use steam of temperatures and/or pressures which are higher; or one can work alternately with steam under variable pressure and/or temperature. For example, one can at first use steam under weaker pressure or with a lesser temperature, and then

change over to higher pressure and higher temperature. At least a small amount of superheating of the steam is advantageous in order to avoid a condensation in the sorption agents.

The active charcoal installations can be divided into several units, as is well known. Into these units one alternately feeds synthesis gas-product; then they are steamed, dried, cooled and again charged with synthesis gas-product. The compounds fixed during the sorption can be fractionally removed by the known methods; e.g. one can drive out carbonic acid before removing the hydrocarbons.

Example 1

Highly desulfurized water gas is converted in a tubular reactor at 190° and under 25 atm. in the presence of a so-called fused iron catalyst; a product is obtained which is a mixture of alcohols and higher hydrocarbons. The catalyst is placed inside tubes of 14 mm. inner diameter; the tubes are surrounded by boiling water. The final gas is cooled to 26° after the synthesis, and thereby, for each m³ of fresh synthesis gas, 121.2 g. of an oily layer separate; pressure is then released and the gas is passed through an active charcoal unit. The latter is charged by regular operations, then regenerated with steam, cooled with air and again charged. It (i.e. the charcoal, Transl.) takes up about ~~22%~~ of its own weight of components consisting of low boiling hydrocarbons which had separated in the form of a separate layer in the condensate of the vapors; and also the oxygen-containing organic substances which were in solution in the aqueous layer of this condensate. For purposes of regeneration, about 5 kg of steam of 150° per kg of adsorbed hydrocarbon layer in the conden-

sate are required. The products still in the vapor phase which are driven off together with the steam, are liquefied in a coil cooler with external cooling. In a separator, the oily layer is separated from the aqueous layer; the hydrocarbon gas which is still not liquefied is caught separately and also liquefied. The water still contains 2.7% of organic substances, essentially low alcohols, acetone, etc. Assuming that this water is not further processed one obtains, per m³ of synthesis gas, only 158 g of total product; if, however, the water is processed, another 5 g of additional product are obtained. For this 184 g of aqueous steam treatment condensate are processed.

Example 2

Following a synthesis as described in Example 1 above, the residual gas now freed from its higher boiling components is passed through an active charcoal unit which is operated as described in Example 1. The charcoal is loaded up to 20% of its own weight. For purposes of regeneration, 5.4 kg of steam for each kg of adsorbed hydrocarbon layer in the condensate are used. In the course of one hour, aqueous condensates were collected separately, after certain definite time intervals and their alcohol contents are as follows:

Alcohol Content of the Aqueous Condensate as Related to the Time of Evaporation

Minutes	Condensate		Alcohols g/m ³ of Synthesis Gas
	kg	%	
0 to 11	2.8	43	0.6
11 to 12	2.3	49	0.5
12 to 14	9.8	25.5	1.2
14 to 17	13.7	15.5	1.0
17 to 22	15.6	5.5	0.4
22 to 27	15.6	4.5	0.3
27 to 32	15.1	2.6	0.2
32 to 37	15.2	0.9	0.1
37 to 42	16.1	0.4	0.05
42 to 47	16.3	<0.1)	can no longer
47 to 60	48.0	<0.1)	be determined
			4.35

Because of the progressively decreasing alcohol concentrations, only the first portions of the condensate (81 g/m^3 synthesis gas), i.e. those up to and including 32 minutes, were processed; the rest is passed into the waste water; the yield is thus increased by 4.2 g/m^3 of synthesis gas.

Example 3

A synthesis is carried out as described in Example 1, but the active charcoal used for the recovery of low-boiling products is regenerated as follows (see enclosed sketch).

Each one of the four sorption units A_1 , A_2 , A_3 and A_4 which are filled with active coal is first subjected to thorough steaming with steam coming from the duct JD; the steam has been generated by evaporation by means of heating with more highly compressed steam. Subsequently, regeneration with fresh steam taken from conduit DD, is carried out. The condensates of the vapors driven off by means of the fresh steam arrive at a collecting vessel (not shown in the sketch), where the oily layer is drawn off and the aqueous layer is passed into an evaporator (not shown in the sketch). Here, the condensate is converted into vapor by means of indirect heating with more highly compressed steam; this vapor is now passed through the duct JD into the next sorption unit for purposes of steaming. The vapors resulting from ~~the treatment with indirectly-generated steam are condensed in a~~ common condenser K, from where the condensate runs into a separator AB. Here, an oily layer will form on top; the aqueous layer is drawn off through the bottom. Both layers are then separately led to the distillation columns D and DK; the former is for the

decomposition of the oily layer, the latter for that of the aqueous layer.

The direct steam (DD) used for the final steaming of sorption vessel A_4 is drawn off and condensed; then it first goes, as indirectly produced steam, through adsorption vessel A_1 , and only then to the final processing. In the same manner, the steam used for the final steaming of adsorption vessel A_1 will be used for the first steaming of A_2 , and so forth. Thus, in each case one uses half directly generated and half indirectly generated steam for the regenerative process.

By this method, another 5 g. of oxygen-containing products, mainly low alcohols, can be obtained; and only 92 g. of aqueous condensate per m^3 of converted synthesis gas have to be distilled.

Patent Claims

1) Process for the preparation of oxygen-containing compounds, besides hydrocarbons, by catalytic reduction of carbon monoxide with hydrogen in the presence of catalysts which contain metals of the iron group, particularly iron; at higher pressure, preferably intermediate pressure; the process is accompanied by the separation of light products by means of adsorbing or absorbing agents which are regenerated with steam; the process is characterized by the fact that after condensation of the steam and of the vaporized low boiling synthesis products, the aqueous layer of the condensate is processed for the purpose of recovering the oxygen-containing compounds.

2) Process according to Claim 1, characterized by the

fact that only the aqueous layer obtained by condensing the first portion of the steam, is processed.

3) Process according to Claim 1 and 2, characterized by the fact that the portion of the aqueous layer which is to be decomposed is used, in the vapor phase, first for the final steam treatment of already partially steamed ad- or ab-sorbing agents, and then for the partial steaming of freshly loaded ad- or ab-sorbing agents.

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