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(54) PROCESS FOR PREPARING GAS MIXTURES CONTAINING HYDROGEN AND CARBON MONOXIDE
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Compounds containing carbon to carbon double linkages are able to react with carbon monoxide and hydrogen in the presence of catalysts, especially of cobalt carbonyl compounds. This reaction, the so called oxo-synthesis or hydroformylation has become an increasingly important technical process for the production of aldehydes and alcohols containing one carbon atom more than the starting olefins (see J. Falbe, *Synthesen mit Kohlenmonoxyd*, Berlin-Heidelberg-New York, 1967, page 3 ff). The said reaction generally results in a mixture of several isomeric aldehydes. Only if olefinically unsaturated compounds which are symmetrical and incapable of isomerization of the olefinic bond are used as starting materials, single aldehydes are obtained. In the oxo synthesis, in addition to the main aldehyde-products various by-products are formed by consecutive reactions of primarily formed aldehydes and alcohols, as for instance higher alcohols, ethers and carboxylic acids, which owing to their distillation characteristics, remain as distillation residues at working up of the oxo reaction mixture. These higher boiling constituents, generally designated as "thick oil" can only partially be converted to valuable products. Furthermore, not all of the several isomeric aldehydes obtained as main product can be further processed with good results. For instance, n-butyraldehyde obtained by hydro-formylation of propylene represents a valuable starting material for numerous technical processes, but it has hitherto not been possible, to use economically the isobutyraldehyde formed in smaller amounts in the same reaction.

It is therefore an object of the invention, to provide a process for utilizing the higher boiling by-products as well as the aldehydes less suitable for further processing to economic advantage. The partial oxidation of the compounds to hydrogen and carbon monoxide containing gas mixtures, which can be used as synthesis gas as for instance for the production of ammonia or for reaction with olefinically unsaturated compounds in the oxo synthesis, appeared promising.

It is known to prepare gas mixtures containing hydrogen and carbon monoxide by partial combustion of hydrocarbons-containing materials with an oxygen containing gas. Such a process is, for example, described in British



Patent Specification 780 120. In the process according to this specification, hydrocarbons are atomized and injected together with an oxygen containing gas and superheated steam into a combustion chamber of distinct construction, care being taken to admix the starting materials intimately. With this known process, hydrocarbons are used as the sole starting material, for example, definite mineral oil fractions; the process is only involved with the conversion of oxygen-free compounds.

It has now been found, that the production of gas mixtures containing hydrogen and carbon monoxide by partial oxidation of carbonaceous compounds with oxygen or an oxygen containing gas in the presence of water vapor at increased temperature and, desirably, increased pressure can be effected with good results, if by-products and waste products of hydroformylation processes, especially isobutyraldehyde are used as carbonaceous compounds and the gasification is effected at a temperature of from 1100 to 1600°C, preferably 1400-1600°C, and a pressure of from 20 to 50, preferably 30 to 40, atm. gauge.

It must be considered as highly surprising, that the various, previously unusable oxygen containing by-products obtained by the hydroformylation of olefinically unsaturated compounds can be converted with the process of the invention to a gas mixture consisting essentially of carbon monoxide and hydrogen and representing a valuable starting material for numerous syntheses. Besides the products indicated hereinbefore, small amounts of saturated hydrocarbons, especially methane, carbon dioxide and carbon black are formed. Surprisingly, the amount of carbon black formed is relatively little, for example, substantially less than in the case of a comparable partial oxidation of naphtha (see Example 1).

The temperature range wherein the gasification process can be carried out may be varied in wide limits but especially good results are obtained in a temperature range of from 1400 to 1600°C. If the starting materials are reacted at lower temperatures, the resulting gas mixture contains increased amounts of hydrocarbons and carbon black.

Although the reaction of the oxygen containing starting materials with oxygen containing gases and water vapor may be conducted at normal

pressure, there is no advantage in this. The working up of the reaction gases, especially the removal of carbon dioxide contained in those reaction gases is best carried out at elevated pressure. Thus, the reaction according to the invention is preferably carried out at pressures between 20 to 50 atm, preferably between 30 and 40 atm.

The oxygen required for the reaction may be pure oxygen or an oxygen rich gas mixture. The complete conversion of the starting materials to carbon monoxide and hydrogen requires 0.4 to 0.6 nm³ oxygen per kg of by-product or waste product respectively.

10 The amount of water vapor to be applied depends upon the carbon content of the starting material. It has proved to be advantageous to apply one mole of water in the form of water vapor per 4 to 6 g-atoms of carbon. On working at the lower limit, carbon dioxide formation is decreased while increasing the amount of water vapor leads to an increase in carbon dioxide formation.

The process of the invention can be carried out in conventional reactors adapted to the production of hydrogen and carbon monoxide by incomplete combustion of hydrocarbons. Oxygen or an oxygen containing gas and carbonaceous starting material are preheated to temperatures of about 350°C in separate preheaters and introduced into the reaction chamber together with steam at a temperature of 350°C.

20 In a particular advantageous embodiment of the invention, the preheated starting materials originating from the oxo synthesis are injected in the form of a hollow conical jet into the reaction chamber. Simultaneously oxygen or oxygen containing gas and water vapor are introduced through tangential openings placed around the circumference of the starting material inlet in such manner that the reactants flow with a rotary motion. This ensures that an intimate intermixing of the reactants, and thus rapid rate of combustion, occurs and the reaction is completed in a short time.

30 An embodiment of an apparatus in which a process according to the present invention may be carried out is shown in the schematic drawing.

Referring to the drawing there is shown a reactor 1 lined with an insulator 2 and a refractory lining 3. The reactor has a nozzle 4, composed

of an inner pipe 5 and an outer pipe 6, flared at their outlet ends. A cone 7 is disposed in the outlet of the inner pipe, and vanes 8 of helical form are disposed in the annulus defined by inner pipe 5 and outer pipe 6. Isobutyraldehyde is introduced through the inner pipe 5 and issues therefrom in a cone-shaped stream. Oxygen and steam are introduced into the annulus between the pipes and issue from the openings between the upper ends of the vanes 8, swirling about the cone of isobutyraldehyde and providing intimate contacting of the two streams. With the use of this device, the substituted hydrocarbon (e.g. isobutyraldehyde), oxygen and steam are contacted for reaction in a reaction zone. The substituted hydrocarbon is introduced into said zone as a diverging annular stream. Oxygen and steam are discharged onto the outer periphery of the diverging annular stream in a whirling mixture for cocurrent movement of annular stream and oxygen-steam mixture through the reaction zone.

The hot gaseous product leaving the reactor is cooled, for example in a heat exchanger and freed from condensed water and carbon black in a separator, whereby the removal of carbon black may be completed by additional injection of water. Carbon dioxide is separated in conventional manner, for example by scrubbing with water under increased pressure or by washing with an alkaline solution. Since the starting materials of the reaction are free of sulfur, an additional desulfurization of the reaction gas is unnecessary.

The invention is illustrated in the Examples.

Example 1

The partial oxidation of by-products and waste products of hydroformylation processes was effected in a testing equipment consisting essentially of the following parts: feed pumps, evaporators, superheaters, splitting reactor, cooler and separator.

The principal part of the testing equipment was the splitting reactor, a tube of 1200 mm length and an inner diameter of 300 mm, which was provided with a refractory rammed lining having a thickness of 50 mm. The compressed mass was heat-insulated by a 12 mm thick surrounding layer of an insulating material. The inner diameter of the reaction space amounted to 76 to 77 mm.

The temperature was measured in the flame cone, in the middle and at the exit of the tube. The development of the flame could be observed through a sight glass provided at the bottom of the reaction space. The starting materials were introduced in gaseous state at the bottom of the reaction space through a stainless-steel combustion-nozzle consisting of a double pipe. The organic starting materials were introduced through the interior tube in form of a hollow conical jet whose apex angle amounted to at most 15° owing to the small diameter of the reaction tube. About 1280 kcal radiant heat were given off by the test reactor per hour. The splitting reactor was at first heated to a temperature of from 1400 to 1450°C with the aid of a town-gas oxygen flame. Thereafter 3,616 kg isobutyraldehyde per hour were evaporated, superheated to 350°C and introduced into the reactor through the interior tube of the combustion-nozzle, while simultaneously a water vapor-oxygen mixture, which had previously been superheated to 350°C in a separate preheater was introduced through the covering tube of the combustion-nozzle into the reaction space. The water-vapor oxygen mixture introduced per hour consisted of 1066 g water-vapor and 2.18 nm³ oxygen. The reaction temperature in the flame amounted to 1500°C and the pressure to 1 atm. The split gas, having a temperature of about 1100°C exiting from the reactor, was immediately quenched with the aid of a cooler and led through a separator in order to remove excess water therefrom. A part of the carbon black formed during the reaction was removed together with the condensed water, the remainder being separated with the aid of filters. The total quantity of carbon black amounted to 1/7 to 1/5 of the amount of carbon black determined in a comparison test using naphtha as starting material.

A gas mixture of the following composition was obtained:

H ₂	44.7 %
CO	48.5 %
CO ₂	5.5 %
CH ₄	1.3 %

From 1 kg isobutyraldehyde respectively the following volumes of gas were obtained:

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H ₂	1.007 nm ³
CO	1.091 nm ³
CO ₂	0.124 nm ³
CH ₄	0.030 nm ³

Example 2

A mixture of by-products and waste products of the hydroformylation of propylene consisting of isobutyraldehyde, thick oil and prerunnings of the butanol distillation corresponding to the following analysis:

10	carbon	65.15 %
	hydrogen	11.50 %
	oxygen	23.35 %
	mole weight	92

was split by partial oxidation with oxygen according to the process described in Example 1. The reaction temperature amounted to 1500°C, the pressure to 1 atm and the throughput to 3.2 kg of the said organic material per hour. 78 g water vapor and 0.570 nm³ oxygen were added per kg starting material.

The primary split material had the following composition:

20	H ₂	47.1 %
	CO	49.1 %
	CO ₂	3.4 %
	CH ₄	0.4 %

From 1 kg organic starting material the following volumes of gas were obtained:

H ₂	1.083 nm ³
CO	1.126 nm ³
CO ₂	0.077 nm ³
CH ₄	0.010 nm ³

Example 3

30 Isobutyraldehyde was autothermically split with oxygen under a pressure of 30 atm gauge following the procedure described in Example 1. The temperature amounted to 1480°C, the throughput to 3.80 kg isobutyraldehyde per hour.

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430 g water vapor and 0.630 nm³ oxygen were added per kg isobutyraldehyde. A split gas of the following composition was obtained:

H ₂	44.7 %
CO	44.5 %
CO ₂	9.0 %
CH ₄	1.8 %

From 1 kg isobutyraldehyde the following gas yields were obtained:

H ₂	1.005 nm ³
CO	1.002 nm ³
CO ₂	0.202 nm ³
CH ₄	0.040 nm ³

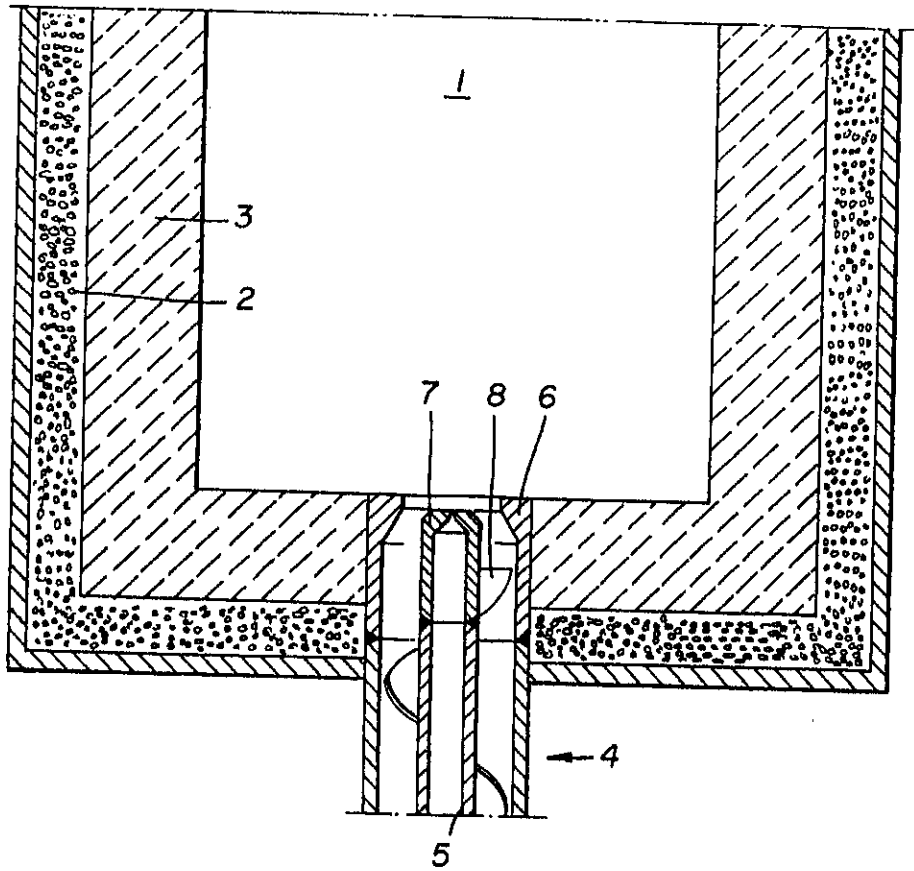
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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Process for producing a mixture of hydrogen and carbon monoxide which comprises contacting by-products of hydroformylation processes, with oxygen and steam at a temperature of about 1100° to 1600°C and a pressure of about 20 to 50 atm gauge for a time sufficient for the by-products, oxygen and steam to react to produce said mixture.
2. Process according to claim 1, wherein said by-product is isobutyraldehyde.
3. In hydroformylation wherein compounds containing carbon to carbon double linkages are reacted with carbon monoxide and hydrogen in the presence of catalyst to form as product an alcohol or aldehyde derivative of the compound having the carbon to carbon double linkage, the said product having one more carbon atom than the compound having the carbon to carbon double linkage, and as by-product a different aldehyde or alcohol, the improvement which comprises: producing a gas mixture of hydrogen and carbon monoxide from said by-product by steps including contacting the by-product with oxygen and steam at a temperature of about 1100° to 1600°C and a pressure of about 20 to 50 atm gauge for a time sufficient for reaction of said different aldehyde alcohol, oxygen and steam to produce said mixture.
4. Process according to claim 3, wherein the said product and the said by-product are aldehydes.
5. Process according to claim 4, wherein the said product is n-butyraldehyde and the said by-product is isobutyraldehyde.
6. Process according to claim 3, wherein the gas mixture of carbon monoxide and hydrogen is recycled to said hydroformylation step.

7. Process according to claim 1, wherein said by-product oxygen and steam are contacted for said reaction in a reaction zone by introducing the substituted hydrocarbon into said zone as a diverging annular stream, and discharging a whirling mixture comprising oxygen and steam onto the outer periphery of the diverging annular stream for cocurrent movement of annular stream and oxygen-steam mixture through the reaction zone.





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