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(54) MANUFACTURE OF OXYGENATED ORGANIC COMPOUNDS

(54) PRODUCTION DE COMPOSES ORGANIQUES OXYGENES

(72) Inventors (Country):	**MATHIAS PIER** (Not Available) **CARL MULLER** (Not Available)
(73) Owners (Country):	**THE BADISCHE ANILIN AND SODA-FABRIK**
(71) Applicants (Country):	
(74) Agent:	
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ABSTRACT:

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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Specification;

TO ALL WHOM IT MAY CONCERN :-

Be it known that we, Alwin Mittasch, Mathias Pier and Carl Müller, Chemists, the first of Ludwigshafen-on-Rhine, the second of Heidelberg and the third of Mannheim, Germany, having jointly invented a certain new and useful improvement in the MANUFACTURE OF OXYGENATED ORGANIC COMPOUNDS, do hereby declare that the following is a full, clear and exact description of the same.

As is known carbon monoxid or dioxid or mixtures of both can be reduced by means of hydrogen or hydrocarbons rich in hydrogen at increased pressure and temperature and under the action of certain catalysts to form liquid hydrocarbons and, ordinarily, certain amounts of oxygenated organic products such as alcohols, aldehydes, acids and the like .

We have now found that the valuable oxygenated compounds, in particular methanol, which up to the present time could only be obtained by charring wood, can be produced with good yields as the sole or chief products, by the reduction of carbon monoxid, or dioxid, provided gas mixtures be employed, on the one hand, containing hydrogen or hydrocarbons in quantities exceeding those of the carbon oxids, i.e. more than one volume of the former to each one volume of the latter, preferably even in quantities corresponding to, or exceeding those calculated according to the formulae:

$$CO + 2\,H_2 = CH_3 \cdot OH \quad \text{and}$$

$$CO_2 + 3\,H_2 = CH_3 \cdot OH + H_2O,$$

and employing at the same time, on the other hand, contact masses containing metal oxids non-reducible under the conditions of working or compounds thereof. The non-reducible oxids may be employed alone or mixed or compounded together or with other substances, either inert or acting catalytically, such as easily reducible metallic oxids or the corresponding metals or with metals of the non-reducible oxids. As instances of contact masses

for the purpose of this invention the oxids, hydroxids or carbonates of the alkali, earth alkali or earth metals, or mixtures or compounds of magnesia, alumina and the like with the oxids of lead, bismuth, thallium, zinc, cadmium, copper, tin, antimony, silicon, boron, titanium are mentioned. Metals of the iron group, however, especially iron, nickel, cobalt, should be present, if any, only in small amounts or in conjunction with other metals, as they may lead to the formation of methane or other hydrocarbons.

The contact masses may be put into the contact furnace without any previous further treatment. As a rule they will be used in the shape of grains or lumps and if mixed catalysts are employed intimate mixtures may be prepared in any suitable manner, for example by simultaneous precipitation or fusion, or by intimately stirring one of the components with the solution, or melt, of the other and supports, such as asbestos may also be employed.

The gas mixture serving for the reaction may contain a high excess of hydrogen (or hydrocarbon) for example one and a half times the calculated quantity by the above formulae or a multiple thereof and besides, it may be purified and dried prior to the reaction.

The desired reaction will ordinarily be carried out between about 300 degrees and 600 degrees Centigrade, but in the case of singularly active masses temperatures even below 300 degrees may be used. The pressure will preferably be kept above 50 atmospheres and may be raised to any desired degree. In general, pressure and temperature should be adapted to the kind of the contact mass actually used; in certain cases very high pressures and/or relatively high temperatures are recommended. The operation can be carried out in a circulating system and with recovery of the heat, by which means the supply of heat can be restricted or even be dispensed with. The original composition of the circulating pure gas is maintained by proper addition of fresh gases. If desired, working may be done without circulating, for example by employing several apparatus in series or by using a single

apparatus with a hot part, containing the catalyst, and a cold part without a catalyst, in which latter the liquid reaction products condense.

The separation of the methanol and other liquid compounds is best effected without releasing the pressure by cooling, which may be assisted by using arrangements furthering the condensation such for instance as towers filled with Raschig rings or other bodies, or the like, or washing with water or other suitable liquids may be employed.

The following examples will serve to further illustrate our invention and the manner in which it may be carried into effect, but the invention is not limited to these examples as the contact masses, gas mixtures, temperature, pressure and other conditions may be varied without departing from the scope of the invention.

Example 1.

A mixture of 3 parts, by volume, of hydrogen and 1 part, by volume, of carbon monoxid is passed, at a pressure between about 500 and 1000 atmosphreres and at a temperature of about 550 degrees Centigrade over a contact mass consisting of potash lime or of a mixture of equal parts of caustic potash and alumina. When the gas mixture, after the treatment, is cooled under pressure, a liquid condenses consisting of methyl alcohol, which may be mixed with other alcohols and sometimes a little water, but no substantial amount of substances of an oily nature. The remaining gas may be used again directly or after suitable replenishment, for instance, it may be passed through another contact vessel. The proportions of the gas mixture may be different, though the hydrogen should, in any event, exceed the carbon monoxid. Instead of, or besides carbon monoxid, carbon dioxid may be used, and besides hydrogen, a hydrocarbon rich in hydrogen, such as methane, may be present. Inert gases, for example nitrogen, may also be present.

Example 2.

A gas mixture composed of about 22 per cent, by volume, of

carbon monoxid, 3 per cent of carbon dioxid, 71 per cent of hydrogen and 4 per cent of nitrogen, is conveyed at a pressure of about 180 atmospheres and at a temperature of 520 degrees Centigrade over magnesium chromate; on cooling the reaction gas under pressure, alcohols, chiefly methanol condense in rich quantity. A granulated mixture of lead chromate with alumina, to which a little caustic potash may be added, is also suitable as a catalyst.

Example 3.

A gas mixture, dry and purified, consisting, by volume, of about 20 per cent of carbon monoxid, 3 per cent of carbon dioxid, 4 per cent of methane and ethane, 70 per cent of hydrogen and 3 per cent of nitrogen is passed at a pressure of 800 atmospheres and at a temperature of between 350 degrees and 400 degrees Centigrade over a contact mass, consisting of magnesium, or zinc, oxid and potassium, or rubidium, hydroxid or carbonate. The liquid reaction product consists chiefly of methanol.

Example 4.

Copper oxid is intimately mixed with powdered aluminium and the mass is ignited at the air, or in an atmosphere of an inert gas. An intimate mixture of copper and alumina results which on passing over it a mixture of 9 parts, by volume, of hydrogen, and 1 part, by volume, of carbon monoxid, gives rise to excellent yields of methanol .

There may also be used mixtures of potassium, caesium, or rubidium, compounds with oxids of, for example, uranium, aluminium, chromium, manganese, or with rare earth, such as cerium, lanthanum, thorium, zirconium, or yttrium oxids, or mixtures or compounds of zinc oxid with alumina, barium oxid, rare earths, or with oxids of chromium, copper, magnesium, molybdenum, manganese, tantalum, titanium, tungsten, or zinc oxid with vanadic acid, or antimony oxid with glucinium oxid, or tungsten threads containing thoria, or metallic molybdenum, or thallium containing alumina may be employed.

A very efficient catalyst is obtained by melting 300 parts by weight of potassium dichromate and introducing, while stirring, 100 parts of zinc oxid which proportions may be varied. On continuing heating, the mass is getting stiff and is then poured on a metal sheet and broken when cool. It may be put into the contact furnace either directly or after leaching out the alkali salt with water, or after a reduction. Instead of zinc oxid, oxids of other metals, for example manganese, thallium, cerium, uranium, thorium, zirconium, or mixtures of them may be introduced into the melt of potassium dichromate.

We claim :

1) The process of producing oxygenated organic compounds by hydrogenating carbon oxids under pressure and at increased temperature which consists in passing a mixture of one volume of a carbon oxid with more than one volume of hydrogen over a contact mass containing a metal oxid non-reducible under the conditions of working .

2) The process of producing methanol which consists in passing, at a pressure of at least 50 atmospheres and at a temperature of at least about 200 degrees Centigrade, a mixture of at least 2 volumes of hydrogen for each one volume of carbon monoxid and at least 3 volumes of hydrogen for each one volume of carbon dioxid over a contact mass containing a metal oxid non-reducible under the conditions of working.

3) The process of producing methanol which consists in passing, at an elevated pressure and temperature, a mixture of one volume of carbon oxids with more than one volume of hydrogen over a contact mass containing several metal oxids, non-reducible under the conditions of working .

4) The process of producing methanol which consists in passing, at an elevated pressure and temperature, a mixture of one volume of carbon oxids with more than one volume of hydrogen over a contact mass containing a metal oxid, non-reducible under the conditions of working, in conjunction with a metal.

5) The process of producing methanol which consists in passing, at an elevated temperature and pressure, a mixture of one volume of carbon oxids with more than one volume of hydrogen over a catalyst containing an oxid of a metal of the first three groups of the periodic system.

6) The process of producing oxygenated organic compounds which consists in passing, at a pressure of at least 50 atmospheres and at a temperature of at least 200 degrees Centigrade, a mixture of one volume of carbon oxids and more than two volumes of hydrogen partly combined with carbon, over a catalyst containing a non-

reducible oxid.

7) The process of producing oxygenated organic compounds which consists in passing, at a pressure of at least 50 atmospheres and at a temperature of at least 200 degrees Centigrade, a mixture of one volume of carbon oxids and morathan two volumes of hydrogen, partly combined with carbon, over a catalyst containing a non-reducible oxid and subjecting the mixture, after treatment, to cooling without releasing the pressure.

8) The process of producing oxygenated organic compounds which consists in passing, at a pressure of at least 50 atmospheres and at a temperature of at least 200 degrees Centigrade, a mixture of one volume of carbon oxids and about two volumes of hydrogen over a catalyst containing a non-reducible oxid and subjecting the mixture, after treatment, to cooling without releasing the pressure, and conveying the residual gas again over a contact mass of the character aforedescribed.

9) The process of producing oxygenated organic compounds which consists in passing, at a pressure of at least 50 atmospheres and at a temperature of at least 200 degrees Centigrade, a mixture of one volume of carbon oxids, substantially carbon monoxid, with about 2 volumes of hydrogen, over a catalyst containing potassium hydroxid and another metal oxid, non-reducible under the conditions of working.

10) The process of producing oxygenated organic compounds which consists in passing, at a pressure of substantially more than 50 atmospheres and at a temperature of at least 200 degrees Centigrade, a mixture of one volume of carbon oxids and more than two volumes of hydrogen over a catalyst containing a non-reducible oxid and not containing iron and nickel.

11) The process of producing oxygenated organic compounds which consists in passing, at a pressure of at least 50 atmospheres

and at a temperature of at least 200 degrees Centigrade, a mixture of one volume of carbon oxids, substantially carbon monoxid, with about two volumes of hydrogen, over a catalysts containing potassium hydroxid and another metal oxid non-reducible under the conditions of working and in the absence of substantial amounts of iron and nickel .

Signed at Ludwigshafen-on-Rhine, Germany, by the said Alwin Mittasch and Carl Müller this 9th day of October 1923.

Alwin Mittasch
Mathias Pier
Carl Müller

Signed at Merseburg Germany, by the said Mathias Pier, this 12th day of October 1923.

~~the ---day of October 1923.~~

Signed in the presence of :

Wilhelm Scherer
Gustav Adolph Reutlinger.