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METHANOL PRODUCTION

Aristid V. Grosse, Haverford, and John C. Snyder,
Darlington, Pa., assignors to Houdry Process
Corporation, Wilmington, Del., a corporation of
Delaware

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This invention relates to methanol and has, as its general object, the provision of novel processes for its production. Other objects will in part be obvious and in part will appear hereafter.

We have discovered, in accordance with the invention, that methanol can be prepared efficiently by decomposing methane sulfonic acid. We have found unexpectedly, that by decomposing methane sulfonic acid, sulfur dioxide is eliminated from the molecule and methanol is formed. Such a decomposition may be effected, we have found, by pyrolysis or thermal decomposition of methane sulfonic acid at moderately elevated temperatures, such as temperatures above 225° C. and below 500° C. to give good yields of methanol.

The methane sulfonic acid for the production of methanol by our process can be obtained by methods known to the art, such as by hydrolysis of methyl sulfonyl halides, by oxidation of methyl thiocyanate, methyl sulfinic acid or methyl mercaptan and the like, but we prefer to obtain it by direct sulfonation of methane with sulfur trioxide as disclosed and claimed in our copending application, Serial No. 673,627 filed of even date herewith. We prefer to use the methane sulfonic acid in the free state; and in any event, the acid should not be in the form of an alkali metal salt since the controlled decomposition of the alkali metal salt to form methanol is difficult if not impossible.

The thermal decomposition may be performed by refluxing the free methane sulfonic acid at atmospheric pressures, the temperature being about 325° C. In performing the refluxing operation, an inert gas such as nitrogen, hydrogen, carbon dioxide or the like may be used to sweep out the methanol and sulfur dioxide or the temperature of the condenser or dephlegmator may be adjusted to allow these products to pass overhead. When a portion of the methanol produced reacts with the undecomposed methane sulfonic acid to form an ester, a fraction composed principally of the ester may be obtained by carrying the decomposition reaction substantially to completion or by separating the ester and the free methane sulfonic acid, as by distillation. The ester can then be easily hydrolyzed to obtain methanol and the free acid, which may then be subjected to decomposition to produce additional methanol or the ester may be both hydrolyzed and the free acid decomposed in the same operation as described below. The process may also be carried out by passing the methane sulfonic acid through a decomposition zone, such as a

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tube either empty or filled with an inert material for heat capacity. This zone is held at a suitable temperature within a preferred range of 300° to 400° C. The methane sulfonic acid may be injected into the reaction zone as a liquid or may enter the reaction zone as a vapor, either alone or in conjunction with an inert gas.

Water, preferably in the form of steam, may be used with the methane sulfonic acid to aid the decomposition or pyrolysis process. When water is present during the pyrolysis, the methane sulfonic acid can conveniently contain the methyl ester thereof ($\text{CH}_3\text{SO}_3\text{CH}_3$), particularly when the methane sulfonic acid is, at least in part, derived from the sulfonation of methane. In a continuous process such as described above, the methyl ester may be added separately to the reaction zone, in which event, water or steam may be added to the methyl ester before it enters the zone. Such mixtures of methyl methane sulfonate and water may be preheated to aid the hydrolysis of the ester. The methyl methane sulfonate is easily hydrolyzed and thus it furnishes additional quantities of methanol and methane sulfonic acid when added to a reaction zone in which methane sulfonic acid is being thermally decomposed to methanol in the presence of steam. When monosulfonated derivatives of methane, such as either methane sulfonic acid or its methyl ester or both, are charged to the thermal decomposition zone, the effluent mixture therefrom may be cooled to a temperature somewhat above the boiling point of methanol, such as about 100° C., in order to condense any unconverted methane sulfonic acid or any high boiling material present or formed in the process, the cooled vapors separated and the methanol and sulfur dioxide recovered.

In accordance with an embodiment of the present invention, we may react methane and sulfur trioxide as described in our application referred to above so as to form monosulfonated derivatives of methane, such as methane sulfonic acid and methyl methane sulfonate, then thermally decompose the monosulfonated derivatives of methane to form methanol and sulfur dioxide as previously described, separate sulfur dioxide from the products of the thermal decomposition, convert the separated sulfur dioxide to sulfur trioxide and react the sulfur trioxide so obtained with further quantities of methane.

The reaction between methane and sulfur trioxide is effected at reaction conditions less severe than those under which methane is completely consumed by oxidation to the carbon oxides, all

as more fully described in our application referred to above. The reaction may be aided by a catalyst, preferably a catalyst of the type known as a sulfonation catalyst. Preferred reaction conditions include the use of catalyst comprising a metal or a sulfate of a metal of group II B of the periodic table, particularly mercury, although the reaction can be effected without the use of a catalyst; reaction temperatures above room temperature, particularly temperatures in the range of 100° to 450° C.; and a wide range of reaction pressures including atmospheric and superatmospheric pressures, the latter generally being below 5000 pounds per square inch. The relative amounts of the reactants, sulfur trioxide and methane, can be varied widely depending on other reaction conditions and the type of products desired.

The sulfonation of methane and the thermal decomposition of the monosulfonated derivatives of methane may effectively be accomplished simultaneously in the same reaction zone by reacting the methane with sulfur trioxide at temperatures above which the thermal decomposition of methane sulfonic acid is moderately rapid, such as temperatures of above 250°, in order to produce methanol in a single step, or somewhat the same results may be effected at lower temperatures, such as 250° C., when the reaction mixture remains in the reaction zone for a longer time (i. e., the contact time is greater). The methanol reacts with any sulfuric acid or sulfur trioxide present to form esters, and hence will be found in the reaction products in this form. However, such methyl esters are easily hydrolyzed and methanol can be easily recovered from the reaction products. In view of the above facts, when methanol is referred to herein, the term will be understood to include either free methanol or methanol in the form of a methyl ester of sulfuric acid.

However, in some cases, the sulfonation and the thermal decomposition may be performed in two zones, as, for example, where lower temperatures, such as temperatures in the range of 200° to 250° C. are used in the sulfonation zone or when it is desirable to separate the products of sulfonation before the thermal decomposition of some of them. Under these conditions, some methanol in the form of an ester may be formed in the sulfonation zone. In the two step process, the sulfur oxides from the sulfonation zone may be separated either before or after the thermal decomposition step, but preferably before if the sulfur trioxide content is high, thus minimizing further oxidation of the methanol present. In any event, the effluent material from the decomposition zone is appropriately processed so as to separate the desired product, methanol.

When the reaction between sulfur trioxide and methane is effected under some reaction conditions, the disulfonated derivatives of methane, methionic acid and its methyl esters, are formed to some extent. If methanol is the desired product, the reaction conditions are generally selected to give as low a production of disulfonated derivatives as is practical in view of the overall economic factors but, in any event, these disulfonated products may be utilized as a source of additional methanol. If the disulfonated products contain esters, a methathetical decomposition of the ester in the presence of water, that is to say a hydrolysis reaction, will form methanol which can then be removed as by steam distillation. If the hydrolysis of the ester and the re-

moval of the methanol is effected at a moderate, elevated temperature, such as temperatures of the order of 100° C., the methionic acid present, including that formed by hydrolysis of the ester, will hydrolyze to form sulfuric acid and methane sulfonic acid. These products can be separated, as by distillation at reduced pressures, and the methane sulfonic acid decomposed to form methanol and sulfur dioxide as described above.

In order to illustrate processes embodying the present invention, and not to be construed as limiting the practice thereof, the following examples are given:

Example I

Methane sulfonic acid, obtained by the hydrolysis of methane sulfonyl chloride and subsequent fractionation under reduced pressure, was refluxed at about 325° C. at atmospheric pressure for one hour. The refluxing operation was performed under dephlegmating conditions such that decomposition products lower boiling than methane sulfonic acid were taken off overhead and subsequently cooled. The condensed liquid decomposition products were distilled, taking off a fraction boiling lower than 100° C. The liquid residue of this distillation was then subjected to steam distillation at about 100° C. Analysis of the portion of the decomposition products boiling less than 100° C. showed that the material consisted at least principally of methanol, in an amount equal to 10% decomposition of the methane sulfonic acid. Sulfur dioxide was shown to be in the gas evolved during decomposition. The residue from the distillation of decomposition products was shown, by the hydrolysis above described, to consist at least principally of the methyl ester of methane sulfonic acid. The methanol formed by the hydrolysis of this ester was equal to about 20% decomposition of methane sulfonic acid originally treated, thus making a total of 30% of the original methane sulfonic acid which had decomposed to produce methanol.

Example II

A run was made in which sulfur trioxide and methane were reacted in a closed vessel in the presence of mercuric sulfate as catalyst under the following conditions:

Temperature, 300° C.
Time of reaction, 40 minutes
Mol ratio of SO₃ to CH₄, 6.9
Pressure (maximum), 1350 lbs./sq. in.

The liquid reaction products were freed of gases and analyzed. The analysis showed that about 28% of the methane originally present had been converted to methanol, whereas a smaller amount, about 17%, had been converted to sulfonic acids of methane.

The methanol produced by the reaction was present in the reaction products as an ester, which hydrolyzed at about 100° C. to yield methanol. Methanol was obtained from the hydrolyzed material by steam distillation.

In the above description, the reaction between sulfur trioxide and methane is, at times, discussed on the basis that the formation of methanol by this reaction is a two step process (i. e., a first step of sulfonation, followed by a second step of pyrolysis of the sulfonated derivative). It is to be understood that the postulation of such a two step process is not intended to exclude the possibility of a single step process in which the methane is oxidized to methanol directly but is

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used because it is convenient when discussing the overall reaction. Any mechanism of reaction should not be construed as a limitation on the present invention. Furthermore, it is to be noted that a similar result (the formation of methanol) is accomplished by either a two step or a single step process, and that in the latter process, although the methane may be directly oxidized to methanol without the intermediate formation of a sulfonated derivative, sulfonated products may be produced by another competing reaction, occurring simultaneously. In the above description and in the appended claims, the term, organic derivative of methane, is used as a term for those derivatives of methane in which at least one hydrogen attached to methane is not replaced, in contradistinction what might be termed the inorganic derivatives or ultimate oxidation products of methane; viz., carbon monoxide and carbon dioxide.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim as our invention:

1. In the production of methanol, the process which comprises decomposing methane sulfonic acid in the free state at temperatures of at least about 225° C. and below 500° C. to form decomposition products and separating methanol from said decomposition products.

2. In the production of organic compounds, the process which comprises thermally decomposing methane sulfonic acid in the free state at temperatures of at least about 225° C. and below 500° C.

3. In the production of organic compounds, the process which comprises thermally decomposing methane sulfonic acid in the free state at temperatures in the range of 300° to 400° C.

4. In the production of methanol, the process which comprises reacting methane and sulfur trioxide under reaction conditions including temperatures in the range of 100° C. to 450° C. and pressures of at least atmospheric to form reaction products comprising esters of methanol, and steam distilling said reaction products whereby methanol is separated.

5. In the production of methanol, the process which comprises reacting sulfur trioxide and methane at temperatures of at least 250° C. and below temperatures above which the methane is completely oxidized to carbon oxides to form reaction products comprising methanol and processing said reaction products to obtain methanol therefrom.

6. The process which comprises reacting sulfur trioxide with methane in the presence of mercury sulfate at temperatures of at least 250° C. and below temperatures above which the methane is completely oxidized to carbon oxides.

7. In the production of methanol, the process which comprises subjecting a mixture comprising methane sulfonic acid in the free state and methyl methane sulfonate to pyrolysis in the presence of water at temperatures of at least 225° C. and below 500° C. to form methanol.

8. In the production of methanol, the process which comprises reacting methane and sulfur trioxide under reaction conditions including temperatures in the range of 100° C. to 450° C. and pressures of at least atmospheric to form reaction products comprising at least one methyl ester

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of sulfuric acid and at least one compound selected from the group consisting of sulfonic acids of methane and methyl esters thereof, steam distilling said reaction products whereby ester hydrolysis occurs and methanol is separated from a less volatile residue, and subjecting at least a portion of said less volatile residue to pyrolysis at temperatures of at least 225° C. and below 500° C. whereby sulfur dioxide and additional methanol are formed.

9. In the production of methanol, the process which comprises reacting sulfur trioxide and methane under reaction conditions including temperatures in the range of 100° C. to 450° C. and pressures of at least atmospheric to form reaction products comprising at least one compound selected from the group consisting of sulfonic acids of methane and methyl esters thereof, processing said reaction products so as to obtain methane sulfonic acid therefrom, and subjecting said methane sulfonic acid in the free state to pyrolysis at temperatures of at least 225° C. and below 500° C. to form methanol.

10. The process of claim 9 in which the reaction of sulfur trioxide and methane is effected in the presence of a catalyst.

11. The process of claim 9 in which the reaction of sulfur trioxide and methane is effected in the presence of a catalyst selected from the group consisting of metals and sulfates of metals of group II of the periodic table.

12. The process of claim 9 in which the reaction of sulfur trioxide and methane is effected in the presence of mercury sulfate.

13. In the production of methanol, the process which comprises reacting sulfur trioxide and methane in a reaction zone under reaction conditions including temperatures in the range of 100° C. to 450° C. and pressures of at least atmospheric to form reaction products comprising at least one compound selected from the group consisting of sulfonic acids of methane and methyl esters thereof, processing said reaction products so as to obtain methane sulfonic acid therefrom, subjecting said methane sulfonic acid in the free state to pyrolysis at temperatures of at least 225° C. and below 500° C. to form methanol and sulfur dioxide, separating said sulfur dioxide from said methanol, converting the separated sulfur dioxide at least partially to sulfur trioxide and returning sulfur trioxide so obtained to said reaction zone and reacting said sulfur trioxide with additional quantities of methane.

14. The process which comprises forming a methyl ester of sulfuric acid by subjecting a reaction mixture comprising methane and sulfur trioxide at a reaction pressure of at least atmospheric pressure and at a sufficiently high temperature within the range of 100° to 450° C. for a time sufficient at such temperature to form a substantial yield of said methyl ester of sulfuric acid.

15. The process which comprises hydrolyzing at least a portion of the reaction products resulting from the process of claim 14 and comprising a methyl ester of sulfuric acid so as to obtain methanol therefrom.

16. The process which comprises reacting sulfur trioxide and methane under reaction conditions including temperatures in the range of 100° to 450° C. and reaction pressures of at least atmospheric pressure to form reaction products comprising a methyl ester of sulfuric acid and at least one compound selected from the group consisting of sulfonic acids of methane and methyl esters thereof, hydrolyzing said methyl ester of

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sulfuric acid so as to obtain methanol, processing said reaction products so as to obtain methane sulfonic acid therefrom, and thermally decomposing said methane sulfonic acid to form sulfur dioxide and methanol.

17. The process which comprises reacting sulfur trioxide and methane at temperatures of at least 250° C. and below temperatures above which methane is completely oxidized to carbon oxides to form reaction products comprising a methyl ester of sulfuric acid and methanol. 10

18. The process which comprises reacting sulfur trioxide and methane at temperatures of at least 250° C. and below temperatures above which methane is completely oxidized to carbon oxides to form reaction products comprising a methyl ester of sulfuric acid, and processing said reaction 15

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products to obtain a methyl ester of sulfuric acid therefrom.

ARISTID V. GROSSE.
JOHN C. SNYDER.

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