[Second Edition.]

PATENT SPECIFICATION.

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COMPLETE SPECIFICATION.

Improvements in and relating to the Catalytic Synthesis of Aliphatic Alcohols.

I, EDWARD CHARLES ROBERT MARKS, a British subject, of 57 & 58, Lincoln's Inn Fields, London, W.C.2, do hereby declare the nature of this invention (a communication to me from abroad by E. I. Du Pont de Nemours and Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, New Castle County, State of Delaware, United States of America), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a catalytic process of synthesizing the higher alcohols of the aliphatic series, that is, those alcohols higher than methanol, and it relates more particularly to a process of producing higher alcohols wherein high space velocities of the reacting gases are employed.

In the continuous form in which this process for the synthetic production of higher alcohols is operated, the exit gas may be recirculated or passed over several bodies of catalyst in series, so that the yield factor of importance is not the per cent. conversion per passage but the space-time yield, by which term is indicated the quantity of product obtained per unit volume of contact mass and per unit of time. The paramount importance of this ratio from the economic standpoint follows from a consideration of the fact that a large part of the cost of the product is made up of fixed charges on the expensive high pressure equipment required.

I have conducted extensive experiments in this field and have discovered a process whereby this important economic factor may be readily controlled to the end that the space-time yield of the higher alcohols may be maintained always at the maximum for the catalyst employed. I have found that the space-time yields of higher alcohols for space velocities above a certain space velocity (depending on the catalyst and other operating conditions) are greater than would be expected from a consideration of the yields at space velocities below that certain space velocity. The space velocity is the volume of gases, measured at standard temperature and pressure, entering the zone of reaction (the catalyst) per unit volume of catalyst per hour. When carbon monoxide and hydrogen are combined in the presence of a catalyst, with a high space velocity of the gases, either substantially pure methanol or a mixture of methanol and higher alcohols may be formed, depending upon the choice of the catalyst used. Known catalysts do not give only higher alcohols, there being present always a greater or lesser amount of methanol depending upon the catalyst and conditions of operation. Generally, the higher alcohol catalyst contemplated in my process is formed by the modification of a methanol catalyst, and the performance of this parent methanol catalyst I have found to be a convenient basis for arriving at a clear concept of the most desirable space velocities of the gases to be employed in carrying out my invention; and to afford a convenient definition of such space velocities and of the most favorable limits thereof.

The reaction by which methanol is formed is known to be a reversible reaction and hence attains an equilibrium, but the reactions by which higher alcohols are formed are not fully understood and may not be reversible in the ordinary sense, so that I prefer to use the methanol reaction as a gauge for specifying the most desirable space velocities in the higher alcohol synthesis. This methanol reaction, therefore, being reversible, will proceed to equilibrium if sufficient time is allowed therefor. Since the process is operated in a continuous manner, the equilibrium time of the reaction may be determined by slowing up the velocity of the gas while maintaining other conditions constant until the composition of the exit gas indicates that conversion to methanol has reached a substantial maximum. I designate the space velocity of the gases at this point as the equilibrium space velocity. This equilibrium space velocity on the parent methanol catalyst for methanol formation serves as a proper basis for defining the preferred space velocity of the gases to be used in the production of higher alcohols, when the parent methanol catalyst is converted to higher alcohol catalyst usually by the addition of a potassium salt.

I have plotted space-time yields of higher alcohols against time of contact, which is, of course, dependent upon space velocity, and I find that the curve slopes upwardly on passing from equilibrium time to minimum time of contact corresponding to the maximum practicable space velocity. Moreover, on passing along this curve in the direction of higher velocities there appears in general to be a critical point beyond which the plotted values of the space-time yields of higher alcohols lie above the smooth curve drawn through the points corresponding to space-time yields at velocities below the critical velocity. I designate the space velocity at this point as the critical space velocity, and I have discovered that this critical space velocity is in general more than five times the space velocity of the gases at the point of equilibrium space velocity of the gases in the production of methanol.

The present invention consists in the process for the synthesis of alcohols of a higher order than methanol, from carbon monoxide and hydrogen, employing as catalyst a methanol catalyst which has been modified by the addition of an alkali metal compound, so as to yield increased amounts of higher alcohols, characterised by operating the process at a space velocity of the reacting gases which is more than five times the space velocity at which a methanol synthesis employing the methanol catalyst will reach substantial equilibrium under the conditions of temperature and pressure used in the process.

In the following embodiments of the invention I show various modes of applying this principle in the production of higher alcohols:

EXAMPLE 1.

A very active contact mass is prepared by the gentle ignition of precipitated basic zinc ammonium chromate and the incorporation of the resulting basic zinc chromite with about 15% of its weight of potassium chromate, after which the mixture is compressed to tablets of a suitable form. A gas mixture consisting of about 35% by volume of carbon monoxide, about 50% of hydrogen, and about 15% of inert gases, and at a pressure of about 280 atmospheres, is passed over one litre of the contact mass contained in a suitable pressure-resisting copper-lined vessel maintained at a temperature of about 450° C. at the various rates of flow indicated below. The table shows the production of both pure methanol and higher alcohols produced per litre of catalyst per hour at various space velocities (previously defined). The percentage of higher alcohols in the crude distillate is also indicated:

Space velocity	Litres Methanol	Litres Higher Alcohol	Higher alcohols as % of total alcohols
10,000	0.27	0.25	48
20,000	0.47	0.36	43
40,000	0.60	0.45	43
70,000	0.70	0.55	44

If the yield of higher alcohols is plotted against space velocity it will be seen that the smooth curve through the zero and the first three points, when extrapolated, lies below the last point. In this case the equilibrium space velocity is about 8,000 litres per hour per litre of catalyst and I prefer to operate the process at 40,000 litres per hour per litre of catalyst.

EXAMPLE 2.

A zinc chromite catalyst containing about six per cent. of potassium in the form of potassium sulphate, when operated as described in Example 1 at about 450° C. but at a pressure of 1,000 atmospheres, yields 0.66 litres of higher alcohols per litre of catalyst per hour together with a considerable volume of methanol when gas of the composition of Example 1 is passed over the catalyst.

I prefer to operate at a space velocity of not less than 100,000 litres of gas per litre of catalyst per hour. The equilibrium space velocity in this case is about 20,000 litres per hour per litre of catalyst.

EXAMPLE 3.

A contact mass prepared by reducing a mixture of one equivalent of zinc oxide and one equivalent of potassium chromate is operated at 475° C. and at a pressure of 225 atmospheres using water gas. With this catalyst I prefer to operate at least 40,000 litres of gas per litre of catalyst per hour. The equilibrium space velocity is about 8,000 in this case.

The application of the aforesaid observations is of the greatest importance from the practical standpoint. Keeping in mind the paramount importance of increasing the space-time yield of product, it is evident, in view of my results, that for any given set of conditions as to temperature of operation, character of contact mass, etc., the maximum space-time yield of higher alcohols, and therefore the minimum cost of product, will be attained by operating at the maximum space velocity suitable to the equipment. It is essential that the space velocity should be increased to a point that is above the critical space velocity. I have found, as already stated, that this critical velocity is generally over five times the equilibrium space velocity for methanol.

I am aware of Specifications numbered 275,345, 258,887, 238,319 and 229,714, and make no claim to what is claimed or described therein.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that, subject to the foregoing disclaimer, what I claim is:—

1. The process for the synthesis of alcohols of a higher order than methanol, from carbon monoxide and hydrogen, employing as catalyst a methanol catalyst which has been modified by the addition of an alkali metal compound, so as to yield increased amounts of higher alcohols, characterised by operating the process at a space velocity of the reacting gases which is more than five times the space velocity at which a methanol synthesis employing the methanol catalyst will reach substantial equilibrium under the conditions of temperature and pressure used in the process.

2. A process as claimed in Claim 1 wherein the catalyst employed is prepared by the gentle ignition of basic zinc ammonium chromate and incorporating therewith 15% by weight of potassium chromate, and a gas mixture of 35% carbon monoxide and 50% hydrogen is contacted with the catalyst at a pressure of about 280 atmospheres and temperature of about 450° C. employing a space velocity of at least 40,000 litres of gas per litre of catalyst per hour.

3. A process as claimed in Claim 1 wherein a gas mixture of 35% carbon monoxide and 50% hydrogen is contacted with a zinc chromite catalyst containing 6% of potassium as the sulphate, at a temperature of about 450° C. and a pressure of 1,000 atmospheres, employing a space velocity of at least 100,000 litres of gas per hour per litre of catalyst.

4. A process as claimed in Claim 1 wherein the catalyst is prepared by reducing a mixture of one equivalent of zinc oxide and one equivalent of potassium chromate, and water gas is contacted with the catalyst at a temperature of about 475° C. and a pressure of about 225 atmospheres, employing a space velocity of at least 40,000 litres of gas per litre of catalyst per hour.

5. The improved process of alcohol synthesis substantially as described.

Dated this 22nd day of June, 1928.

MARKS & CLERK.

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