[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Production of Olefines.

We, Alfred William Nash, of "Hapri", Warwick Road, Solihull, Warwickshire, Arthur Riley Bowen, of 63, Bromyard Road, Worcester, and Oliver Cecil Elvins, of 701, Coventry Road, Birmingham, all British subjects, do hereby declare the nature nature of this invention to be as follows:—

The object of this invention is to utilise mixtures of carbon monoxide and hydrogen, or commercial gaseous mixtures containing carbon monoxide and hydrogen, such as water gas, for the synthetic production of olefinic hydrocarbons and oxygenated organic compounds.

It is known that carbon monoxide and hydrogen at high temperatures in the presence of catalysts and under high pressure produce hydrocarbons of the paraffin series and oxygenated compounds of these hydrocarbons, together with smaller quantities of olefines and oxygenated compounds derived from them.

In the process forming the subject of this invention, a mixture of carbon monoxide and hydrogen at atmospheric pressure is passed over a heated catalyst at temperatures about 280° Cent. (the use of high pressure being dispensed with); the catalyst consists of a mixture of the reduced oxides of cobalt, manganese and copper, and is used in a granular state preferably contained in a copper tube (of suitable form) which is maintained at a temperature of 280° C.

The catalyst is prepared by known methods, such as the precipitation of the oxides, or of the mixed oxides, or the thermal decomposition of salts such as the nitrates or carbonates, to produce the oxides, either separately or from a mixture of these salts in suitable proportions. For example a mixture of the nitrates of copper, cobalt and manganese may be used in such proportions that after precipitation or decomposition by heating a mixture of the oxides containing 30 parts of copper oxide, 60 parts of cobalt oxide and 45 parts of manganese oxide is obtained. The prepared oxides may be fused and the fused mass granulated before reduction in a current of hydrogen at a temperature of 400° to 420° C. To obtain good results a relatively large amount of the catalyst is required, and for this reason the granular form is more advantageous. After use the catalyst can be revived either by passing a current in steam over it or by oxidation and subsequent reduction.

When a mixture of carbon monoxide and hydrogen at atmospheric pressure at a temperature of 280° Cent. is passed over the catalyst above described a mixture of gaseous liquid and solid olefines is produced together with saturated hydrocarbons and smaller quantities of oxygenated organic compounds. To obtain good results the proportion of the carbon monoxide to the hydrogen should be high. If water gas is used an addition of carbon monoxide is made to obtain the necessary proportion to the hydrogen. The relative yields of olefines, saturated hydrocarbons and oxygenated organic compounds naturally vary with the conditions, such as the catalyst, the composition of the gas mixture and temperature.

The oxygenated organic compounds obtained consists of acids and compounds containing the carbonyl group.

The gaseous olefines may be directly converted into alcohols by well known methods. The liquid products are absorbed in activated charcoal, and subsequently steamed out. The oxygenated organic compounds are found in the aqueous layer so obtained and can be separated by the usual fractionation processes.

Dated this 9th day of March, 1927.

KINGS PATENT AGENCY LIMITED,
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COMPLETE SPECIFICATION.

Production of Olefines.

We, Alfred William Nash, of "Hapri", Warwick Road, Solihull, Warwickshire, Arthur Riley Bowen, of 63, Bromyard Road, Worcester, and

Oliver Cecil Elvins, of 701, Coventry Road, Birmingham, all British subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The object of this invention is to utilise mixtures of carbon monoxide and hydrogen, or commercial mixtures containing carbon monoxide and hydrogen, such as water gas, for the synthetic production of olefinic hydrocarbons.

It is known that carbon monoxide and hydrogen at high temperatures in the presence of catalysts, and under high pressure, produce saturated hydrocarbons of the paraffin series and oxygenated compounds of these together with smaller quantities of olefines and oxygenated compounds derived from them.

It is also known (British Patent Specification No. 255,818) that paraffin hydrocarbons with more than one carbon atom can be produced from gases containing oxides of carbon and hydrogen, heated in the presence of methane-forming catalysts at ordinary pressure, an example of such a catalyst being a mixture of zinc oxide and finely divided iron. Morever it is also known (British Patent Specification No. 282,573 that gas mixtures containing approximately equal proportions of carbon monoxide and hydrogen, such as can be produced from lump semi-coke, may be passed over a catalyst consisting of finely divided iron or metals with and without promoters, at atmospheric pressure to form paraffin hydrocarbons.

We have discovered that good yields of olefines can be produced from mixtures of carbon monoxide and hydrogen, in which the carbon monoxide is present in excess of the hydrogen when passed over a suitable catalyst hereinafter described, at temperatures between 280° and 300° C. and at atmospheric pressure. If the gases are in the same proportion or if hydrogen is in excess then the products are, as is known, mainly paraffin hydrocarbons. Any substantial increase of temperature above 300° C. results in reducing the olefine yield to negligible quantities in comparison with a vastly disproportionate increase in the paraffin yield. The best results have, so far, been obtained by the employment of a catalyst as hereinafter described. Further it will be seen from the examples given that when the carbon monoxide fraction of the mixed gases falls below 50 per cent., then, again the olefine yield decreases to unimportant quantities. Therefore, for the purpose of the invention the carbon monoxide must be in excess of the hydrogen in the gaseous mixture.

The catalyst consists of a mixture of the oxides of cobalt copper and manganese, the mass being reduced in a current of hydrogen at the appropriate temperature (400°—420° C.) before use. The catalyst is employed in a granular state, preferably in a copper tube (of suitable form) which is maintained at a temperature of 280° to 300° C.

The catalyst is prepared by known methods such as the precipitation of the oxides or of the mixed oxides, or by the thermal decomposition of salts such as the nitrates or carbonates to produce the oxides, either separately or from a mixture of these salts in suitable proportions. For example, a mixture of the nitrates of copper, cobalt and manganese may be used in such proportions that after precipitation or decomposition by heating, a mixture of the oxides containing 30 parts by weight of copper oxide, 60 parts of cobalt oxide, and 45 parts of manganese oxide is obtained. The prepared oxides may be fused and the fused mass granulated before reduction in a current of hydrogen at a temperature of 400° to 420° C., or suitable temperature. The use of the fused oxide catalyst provides a hard granule suitable for large scale work. To obtain good results a relatively large amount of the catalyst is required, and for this reason the granular form is more advantageous. After use the catalyst can be revived either by passing a current of steam over it or by oxidation and subsequent reduction.

When a mixture of carbon monoxide and hydrogen, with carbon monoxide in excess, at atmospheric pressure, and at a temperature of 280°—300° C. is passed over the catalyst above described a mixture of gaseous, liquid and solid olefines is produced, together with saturated hydrocarbons and smaller quantities of oxygenated organic compounds. If water gas is used an addition of carbon monoxide is made to obtain the necessary proportion to the hydrogen. The relative yields of olefines, saturated hydrocarbons and oxygenated organic compounds naturally vary with the conditions, such as catalyst, the composition of the gas mixtures and the temperature.

The following examples illustrate the manner in which this invention may be carried out, but it is not confined to these examples.

Example I.

A gas mixture containing 55.7 per cent. carbon monoxide and 43.4 per cent. hydrogen (the remaining 0.9 per cent. being carbon dioxide and nitrogen) passed at a speed of 4.2 litres per hour, through a reaction tube of approximately 1.5 sq. cm., at atmospheric pressure, at a temperature of 286° C. over the catalyst (prepared by the ignition of nitrates so that the resulting mixture had the composition 60 parts by weight cobalt oxide, 30 parts copper oxide and 45 parts manganese dioxide, reduced at 400°—420° C.) yielded among the gaseous products 3.6. per cent. olefines and 6.6 per cent. saturated paraffins. When the carbon monoxide was reduced to 31 per cent. and 26 per cent. respectively of the mixed gases, the yields of olefines and paraffins were 1.5 per cent. and 11.8 per cent. and 0.4 per cent. and 19.8 per cent. respectively. This indicates that carbon monoxide must be in excess of the hydrogen to obtain the result aimed at by the present invention.

EXAMPLE II.

A gas mixture containing 53.1 per cent. carbon monoxide and 46.5 per cent hydrogen and traces of other gases passed, at a speed of 3.5. to 5 litres per hour through a tube as in Example I and over the same catalyst as in Example I, at various temperatures gave the following results :—

Temperature.	Olefines	Paraffins.
280° C.	2.1 per cent.	4.9 per cent.
305° C.	2.7 per cent.	15.9 per cent.
317° C.	1.1 per cent.	13.4 per cent.

which proves that temperatures of about between 280° and 300° C. are most suitable for a good yield of olefines, and that temperatures, such as 317° C., give a decidedly smaller yield of olefines, rendering the process impracticable for the purpose in view.

The liquid products of reaction can be condensed out or absorbed in such substances as activated charcoal etcetera.

The olefinic and unsaturated compounds are evident in the liquid and solid reaction products by their appreciable bromine absorption numbers and also by their darkening in colour when exposed to light. These can also be separated by known processes.

The exit gas obtained when a mixture containing 56 per cent. carbon monoxide and 44 per cent. hydrogen is used, after the removal of the olefines, paraffins and the by-product carbon dioxide, contains carbon monoxide and hydrogen with the former in a lower ratio to the latter than in the initial gas mixture. This exit gas may be re-utilised for the process after the necessary adition of more carbon monoxide.

The gaseous olefines may be directly converted to valuable alcohols by well known methods.

Having now particularly decribed and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is :—

1. The production of olefines by passing a mixture of carbon monoxide and hydrogen containing excess of the former, at atmospheric pressure and at tempertures between 280°—300° C. over a catalyst consisting of a reduced mixture of the oxides of cobalt, copper and manganese, preferably in the granular state.
2. A process according to Claim 1 wherein the catalyst employed is prepared substantially as herein described.

Dated this 3rd day of May, 1928.
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