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PROCESS FOR SELECTIVE OXIDATION OR
DEHYDROGENATION OF PETROLEUM HY-
DROCARBONS

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In my applications Ser. Nos. 276,412 of May 29, 1939; 285,519 of July 20, 1939, and 324,341 of March 15, 1940, I described processing for the selective oxidation or dehydrogenation of petroleum and chlorinated petroleum hydrocarbons, more especially oils such as gas and fuel oils of higher specific gravities, by oxygen in concentrations less than that ordinarily occurring in air or, that is, under approximately twenty percent, and an inert gas, as nitrogen, with the use of ferric oxide, ferric hydroxide and cupric oxide, used either singly or in combinations, as the catalytic materials. The catalyst or catalytic combination was supported on asbestos fibre and suitably bound thereto by calcium silicate deposited on the asbestos fibre after the same had been thoroughly mixed or commingled with the catalyst.

In the present application the same general basis of processing is employed, but it has been further evaluated or extended to include dehydrogenation or selective oxidation of hydrocarbon gases, more especially those given off as by-products from the "cracking" of crude petroleum or other petroleum oils to produce gasoline.

The butane and butylene gases, with which experimentation was more exhaustively carried out, consisted of mixtures of these hydrocarbon gases purchased on the market, and condensed and fractionated, applicant was given to understand, from waste gases secured from the cracking of crude petroleum oils. These gases, according to analyses furnished applicant, were not pure butanes or butylenes but also contained smaller percentages of higher and lower hydrocarbons, such as pentanes, pentenes, amylenes, propanes and propylenes, etc. In other words, they represented gas mixtures which may be secured cheaply for commercial operations.

The reaction chamber used by me in which to establish dehydrogenation or selective oxidation was a chrome-nickel-iron tube about six feet long, one and one-half inches internal diameter and two and three-eighths inches external diameter. The tube was heated by electric resistance furnaces with suitable rheostatic control to give the desired operating temperature.

Both the oxidizing gas and hydrocarbon gases were fed from suitable steel reservoirs, tubes or cylinders, and the flow controlled by needle valves. The hydrocarbon gases were maintained under about five hundred pounds pressure, established by nitrogen gas, contained in the upper portion of the supply tube, under which pressure the hydrocarbon gases are liquefied. The

latter were mixed during flow with the oxidizing gas before entering the reaction tube. The mixing chamber, consisting of a steel T, was suitably warmed in order to maintain the gas as such without danger of possible liquefaction under the superatmospheric operating pressures used in experimentation.

A range of pressures from about one pound to three hundred pounds superatmospheric pressure and temperatures of from one hundred to four hundred degrees centigrade were used during the experimentation and from five to twenty percent of oxygen was used with nitrogen as the residual or inert gas. Naturally, other inert gases might be used in place of nitrogen. As in his other experimentation, applicant found a five to ten percent oxygen content as most suitable or advantageous for the selective oxidation of the waste petroleum hydrocarbon gases under consideration. About a seven percent oxygen content, as also used in his earlier experimentation, was established as possibly the most suitable.

Applicant has described the use of ferric hydroxide and cupric oxide as a catalytic combination in earlier applications, the percentages of the respective constituents being used in varying proportions dependent on the specific gravity of the oil used for dehydrogenation. For the present hydrocarbon gases, selective oxidation was carried out with the use of ferric hydroxide alone, with ferric hydroxide, cupric oxide and cupric hydroxide. One experiment was also carried out with the use of about eighty-five percent ferric hydroxide and fifteen percent cuprous oxide, but the latter was found less advantageous than when using the same percentage of cupric oxide.

As an example of my experimentation, about four hundred c. c. of "butylene" gas per minute, measured at atmospheric pressure, and mixed with a flow of about three liters per minute of the oxidizing gas, consisting of seven percent oxygen and ninety-three percent nitrogen, were passed through the reaction tube maintained at about two hundred to two hundred and twenty-five degrees centigrade and at from fifteen to thirty pounds superatmospheric pressure with ferric hydroxide used as the catalyst. The latter consisted of two hundred grams of finely divided ferric hydroxide supported on about one hundred and fifty grams of medium length asbestos fibre. The initial oxidizing gas had an oxygen content of seven and a half percent. The residual or spent gas, that is, the gas given off after completion of selective oxidation, contained

about one percent of carbondioxide and one and a half percent of free oxygen. In other words, about five percent of the gas content, or sixty-six percent of the oxygen used reacted or combined with the hydrogen to give water. For complete oxidation of a $-\text{CH}_2$ group, there would be used half as much oxygen in synthesis of water as in production of carbon dioxide, and for a $-\text{CH}_3$ group there would be used three-fourths as much. Thus the actual percentage of oxygen used selectively for dehydrogenation in the first case was the following:

$$\frac{7\frac{1}{2} - 1 - \frac{1}{2} - 1\frac{1}{2}}{7\frac{1}{2}} = 60\%$$

An experiment in every way similar to the above, except that the catalytic combination consisted of eighty-five percent ferric hydroxide and fifteen percent of cupric oxide showed that practically eighty percent of the oxygen had acted selectively or to establish dehydrogenation. One-half percent of carbondioxide and three-fourths of a percent of oxygen were found in the residual gas.

When using a gas mixture, consisting mostly of butanes, it was found that a catalytic mixture consisting of ferric hydroxide and cupric hydroxide in place of copper oxide acted more efficiently with regard to dehydrogenation. A mixture consisting of two parts by weight of ferric hydroxide to one part by weight of cupric hydroxide proved to be a very effective catalytic combination. Cupric hydroxide, however, cannot be employed for temperatures above three hundred degrees, as it then decomposes to the oxide. With a flow of about three liters per minute of the oxidizing gas consisting of seven and one-half percent of oxygen and ninety-two and one-half percent of nitrogen at about two hundred and twenty-five degrees centigrade and twenty pounds superatmospheric pressure, and a flow of about one liter per minute of the butane gas practically no carbon dioxide, or so small a percentage as to be within the limits of experimental error, was found in the residual gas. The latter showed a content of about one and one-half percent of oxygen, so that practically eighty percent of the oxygen had reacted selectively toward dehydrogenation. On reducing the flow of the oxidation gas to two liters per minute, measured at atmospheric pressure and temperature, neither oxygen nor carbon dioxide were found in the exit gas, so that the oxygen had acted practically one hundred percent selectively toward dehydrogenation.

For most effective dehydrogenation the oxidation gas should be forced into the reaction tube at several points separated from one another, at suitable spacings along the path of travel of the butane gas. The higher the percentage of the butane gas relative to the oxidation gas, the more perfect the dehydrogenation relative to complete oxidation. Such findings are of course in accord with what we should expect from analyses of the equilibria in question. With very small percentages of the butane gas relative to the oxidation gas, even under the operation conditions described, formation of carbondioxide and water showed that only, what we might term, actual combustion had occurred without appreciable selective oxidation or dehydrogenation.

A heavy fuel oil of about 0.9 specific gravity was also selectively oxidized when using the ferric hydroxide-copper hydroxide catalyst. The oil was pumped through the reaction tube at a rate

of about one hundred grams per hour with a flow of gas of about three liters per minute. The pressure used was about one hundred and twenty-five pounds and the operation temperature between two hundred twenty-five and two hundred and fifty degrees. Practically no oxygen or carbondioxide was found in the residual gas, so that the oxygen had acted a hundred percent selectively. When used in a lighter fuel oil of about 0.82 specific gravity, an operation pressure of about seventy pounds was found more advantageous. It will be noted that fifteen to thirty pounds superatmospheric pressures were used with the butane gas mixtures. Thus it will be seen that the heavier the hydrocarbons, or the greater their molecular weights, the higher the operation pressure used for the most advantageous dehydrogenation results.

In place of ferric hydroxide, ferric oxide was used as a catalytic combination in conjunction with cupric hydroxide. The dehydrogenation of an 0.84 sp. gr. fuel oil at seventy pounds pressure and at about two hundred and thirty-five degrees was carried out with the use of this catalytic combination and relatively good results were obtained, although ferric hydroxide appears unquestionably superior to the oxide, when used with copper hydroxide.

The mixture of butylenes secured by our selective oxidation or dehydrogenation methods may, of course, be directly condensed or polymerized, more especially with the aid of solid copper hydrogen phosphate as the catalyst, to octanes, or gasoline, in the presence of the inert gas, or that is, without separating them by compression or fractionation from such inert gas. Applicant has carried out many such condensations in the presence of nitrogen gas at superatmospheric pressures and very successfully. Of course, such steps are not pertinent to this application and the consideration is mentioned only insofar as to disestablish the necessity of the separation step and to establish that direct polymerization of the butylenes has been carried out in the presence of the inert gas.

Applicant noted an experiment carried out with the use of cuprous oxide and ferric hydroxide. Other experiments with the use of the reduced oxides and hydroxides of copper and iron have been carried out and are at present being conducted, but the optimum percentages of the ferrous and cuprous salts have not yet been well established, as is the case with the corresponding ferric and cupric salts. Hence applicant has not included any of the data from these preliminary experiments.

Applicant believes that he has now described his processing in reasonable detail through having given examples of the more preferred processing used. Examples of the unprofitable processing or experimentation would probably not aid by their disclosures and take up only undue space.

Applicant finally will give the method of binding the catalyst to the asbestos fibre. The catalyst, consisting of finely divided or powdered iron oxides or hydroxides and copper oxide or hydroxide, and asbestos fibre, were first thoroughly mixed or commingled by shaking together in a closed vessel. As an example of the treatment employed, one hundred and fifty grams of a so-called medium length asbestos fibre were thoroughly mixed with one hundred and fifty grams of powdered ferric hydroxide and seventy-five grams of cupric hydroxide.

About sixty grams of a forty percent sodium silicate solution were mixed with five hundred grams of water. The asbestos fibre was then thoroughly commingled or impregnated with a sodium silicate solution and then with a calcium acetate solution. It was then dried by heating at about one hundred and fifty degrees. It was subsequently washed with hot water three times, with filtering between each washing, to free from sodium acetate, and dried.

Sodium silicate alone does not establish the binding quality between the catalysts and asbestos fibre carrier. Calcium chloride was used in place of calcium acetate, but the sodium chloride formed effects the properties of the catalyst unfavorably.

I claim—

1. In a process for the dehydrogenation of hydrocarbons of a class consisting of the hydrocarbon gases above methane and delivered as waste gases from petroleum oil cracking, the step of subjecting the said hydrocarbons to treatment with a mixture of oxygen and an inert gas in which the percentage of oxygen in the said mixture is less than twenty, namely that normally contained in air, the oxygen being present in amount sufficient only to react substantially with all of the hydrogen liberated during the reaction, at superatmospheric pressures and temperatures between one hundred and four hundred degrees centigrade, in the presence of a catalytic combination consisting of the oxides and hydroxides of iron and of copper.

2. In a process for the dehydrogenation of hydrocarbons of a class consisting of the hydro-

carbon gases above methane and delivered as waste gases from petroleum oil cracking, the step of subjecting the said hydrocarbons to treatment with a mixture of oxygen and an inert gas in which the percentage of oxygen in the said mixture is less than twenty, namely that normally contained in air, the oxygen being present in amount sufficient only to react with substantially all of the hydrogen liberated during the reaction, at superatmospheric pressures and temperatures between one hundred and four hundred degrees centigrade, in the presence of a catalytic combination consisting of the oxides and hydroxides of iron and of copper, supported on asbestos fibre and cemented to the said fibre by calcium silicates.

3. In a process for the dehydrogenation of hydrocarbons of a class consisting of the hydrocarbon gases above methane and delivered as waste gases from petroleum oil cracking, the step of subjecting the said hydrocarbons to treatment with a mixture of seven percent oxygen and ninety-three percent nitrogen, the oxygen being present in amount sufficient only to react with substantially all of the hydrogen liberated during the reaction, at about twenty pounds superatmospheric pressure and one hundred and fifty to three hundred degrees centigrade in the presence of a catalytic combination consisting of about two parts by weight of ferric hydroxide and one part by weight of cupric hydroxide supported on asbestos fibre and cemented to the said fibre by calcium silicates.

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