

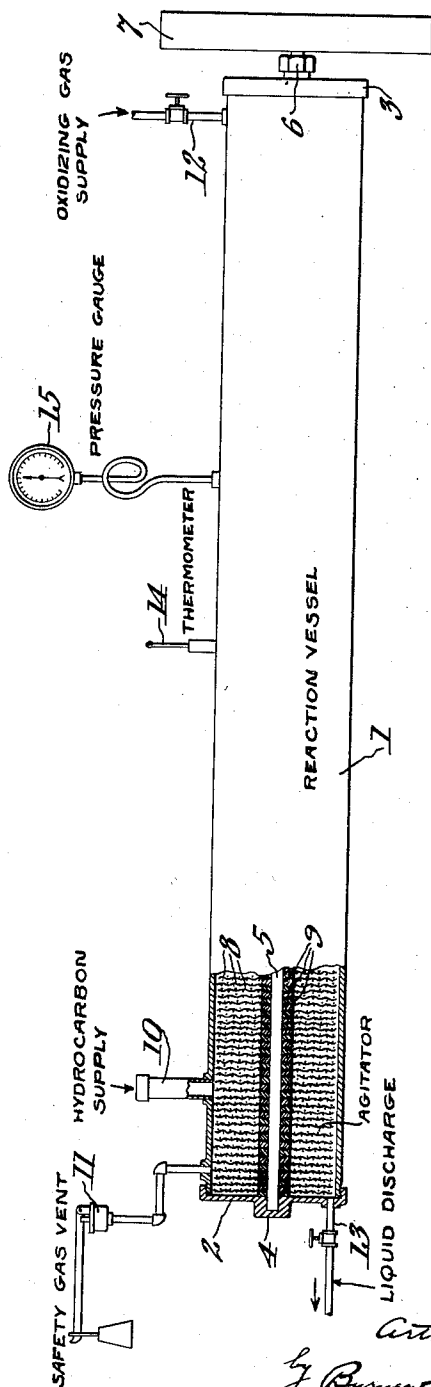
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OXIDATION OF HYDROCARBONS

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OXIDATION OF HYDROCARBONS.

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This invention relates to a process for the controlled oxidation of hydrocarbons for the production of useful oxidation products, such as, alcohols, aldehydes and acids.

5 I have found that the hydrocarbon of the aliphatic series, such as are found in petroleum oils or distillates, and aromatic hydrocarbons having an aliphatic side chain attached to the nucleus, such as the hydrocarbons occurring in the products of the destructive distillation of coal and other organic materials, may be oxidized under properly controlled conditions of temperature and pressure by means of oxygen or
10 air or other oxidizing gas or agent with or without a catalytic agent or oxygen carrier to produce economical yields of useful oxidation products.

The invention therefore relates to the process of oxidizing hydrocarbons generally under controlled conditions which will be described hereinafter in connection with the description of a process of oxidizing petroleum hydrocarbons to form organic acids
20 for which oxidation the process is more particularly designed.

A feature of the invention is the controlled or selective production of either the simple acids, that is, acids containing only the carboxyl group, and the hydroxy acids, that is, acids containing both the carboxyl group and one or more hydroxyl groups.

The accompanying drawing illustrates apparatus suitable for carrying out the process. The apparatus comprises in general a reaction vessel provided with suitable controlled openings for the introduction of the hydrocarbon and the oxidizing agent and for the removal of liquid and gas. The reaction vessel also is provided with means for indicating the temperature and pressure, a safety vent to relieve excessive pressure, means for heating the contents of the reaction vessel and means for agitating the contents of the reaction vessel to secure intimate contact between the hydrocarbon and the oxidizing agent.

Referring to the drawing, 1 is a cylindrical vessel which may be formed of any suitable material capable of withstanding the heat and pressure employed, preferably an iron or copper or other metal pipe arranged horizontally. The pipe 1 is provided with end closures or caps 2 and 3 which are

conveniently attached by means of screw threads. The cap 2 has a lug 4 adapted to rest on a supporting frame, not shown. The inner surface of the cap 2 carries a bearing for the rotatable longitudinal shaft 5. The shaft 5 extends through the axis of the pipe 1 and through the stuffing box 6 carried on the cap 3. The projecting end of the shaft 5 carries a pulley 7 or other suitable means for rotating the shaft. Mounted on the shaft 5 are a large number of parallel spaced discs of wire screen 8. The discs 8 preferably are positioned close together being spaced by washers 9 as illustrated, and are circular and extend close to but to not touch the walls of the pipe 1. The discs 8 are made of iron, copper or other suitable metal or material and preferably are formed of wire screen although they may be perforated discs or plates of sheet metal or other material. 10 is a filling tube provided with a closure through which hydrocarbon is supplied to the reaction chamber. 11 is a safety gas outlet which is adjustable for use to maintain a constant maximum pressure in the apparatus. 12 is the oxidizing gas supply inlet pipe and 13 is the draw-off pipe for the liquid product of the reaction. 14 is a thermometer. 15 is a pressure gauge. Suitable means, not illustrated, are provided for heating and cooling the reaction vessel and its contents, for instance, an ordinary oil or gas burner positioned under the pipe 1 for heating and a water sprinkling pipe above the tube 1 for cooling.

The process is carried out as follows:

The cylinder is charged about half full, that is, up to the level of shaft 5 with the hydrocarbon to be oxidized. The hydrocarbon employed will depend upon the product desired. For instance, if it is desired to produce the lower fatty acids including formic, acetic, propionic, etc. a hydrocarbon mixture containing the corresponding hydrocarbons including methane, ethane, propane, etc. will be used. The reaction chamber is then closed and the agitator started to revolve, the contents of the vessel being heated and air or other oxidizing gas supplied. The rate of rotation of the agitator, that is, the shaft 5 and discs 8 may be regulated as desired to produce intimate contact between the liquid and gas, but must

not be so fast as to work the liquid contents of the vessel into a spray or foam. In experimental apparatus in which the tube 1 is about 8 inches in diameter and the discs 8 are made of screen wire of about #6 mesh #18 iron wire, the rate of rotation may vary from 20 to 100 revolutions per minute, preferably about 30 revolutions a minute. The temperature, pressure, rate of supply of oxidizing gas and rate of rotation of the agitator shaft preferably are regulated so that the process is self-sustaining, that is, the reaction continues without the further application of heat, the heat necessary for the reaction being supplied by the reaction itself.

The self-sustaining reacting conditions for any particular hydrocarbon or hydrocarbon mixture, oxidizing gas, size of apparatus etc., are readily determined. Self-sustaining reacting conditions are indicated when the temperature of the reaction vessel remains constant without the application of heating or cooling medium. The rate of reaction can be varied in the following ways: The pressure within the reaction vessel may be increased by adjustment of the gas outlet 11. Increase in pressure increases the rate of reaction. The rate of reaction is increased also by increasing the agitation from the minimum, that is, no agitation up to the point at which undesirable foam or spray is formed, this condition being indicated by the discharge of liquid hydrocarbon through the gas outlet 11. The rate of reaction is increased also by increase in temperature and within reasonable limits by increase in the rate of supply of oxidizing gas. If the oxidizing gas used is pure oxygen the rate of reaction is nearly directly proportional to the rate of gas supply, but if air is used the inert nitrogen gas present exerts a cooling effect and for this reason it may be found that an excessive supply of air will cool the reaction mixture and thus retard the reaction.

I have found that the reaction conditions may be practically standardized for a wide range of hydrocarbons since a fairly wide variation in the composition of the hydrocarbon requires only a very small variation in the reaction conditions and in many cases no change in the reaction conditions is required. On a rather wide range of petroleum distillates, among which are mentioned a 32° Bé spindle oil distillate and a 41° Bé distillate from Pennsylvania crude oil, substantially the following reacting conditions have been employed. Rate of rotation of agitator 30 revolutions per minute; temperature 120° C. to 130° C.; pressure 150 pounds per square inch; air supply at a rate sufficient that the oxygen content of the air is reduced about 40 percent. Some adjustment of reaction conditions of course is ad-

visable. For instance, in treating a more volatile hydrocarbon a higher pressure and a lower rate of air supply should be used to minimize volatilization of the hydrocarbon while in treating a hydrocarbon of high boiling point a lower pressure and a higher rate of air supply may be used. I have found that the pressure may vary from 100 to 200 pounds per square inch but in general a pressure of about 180 pounds to the square inch is the maximum pressure at which the process may be carried out without cooling. At above 180 pounds pressure the temperature tends to rise rapidly. A pressure of about 100 pounds is required to make the process self-sustaining under other appropriate reaction conditions. As stated, I prefer a pressure of about 150 pounds. If gas more rich in oxygen than air is employed the temperature, pressure, and rate of agitation, particularly the pressure, should be correspondingly reduced, and if gas less rich in oxygen is employed the temperature, pressure and rate of agitation, particularly the pressure, should be increased.

I have found that by operating with petroleum distillates of the kind mentioned and under the preferred reaction conditions described I am able to form organic acids capable of forming water soluble sodium salts at the rate of about 5 percent per hour calculated on the weight of the batch of oil treated.

For the production of the simple carboxylic acids as the principal product the oxidation should not be carried beyond the point at which the total acid content of the hydrocarbon mixture treated is about 20 percent. When the simple fatty acids are desired the oxidation is carried to this point and the batch is withdrawn from the apparatus and treated with a suitable alkali, for instance, a water solution of caustic soda. The acids dissolve in the water solution which is separated and the oil is returned to the apparatus for further treatment. It will be apparent that the process may be made continuous by continuously supplying hydrocarbon at one end of the pipe 1 and withdrawing the reaction product at the other end, removing the acids as described and returning the separated oil to the pipe 1. The fatty acids are recovered from the alkali solution and purified in the well known manner.

For the production of the hydroxy acids as the principal product the oxidation of a batch of hydrocarbon is continued until say 80 percent of the hydrocarbons are converted to acid. A separation of the hydroxy acids from the reaction mixture may be accomplished by gravity because the hydroxy acids are only sparingly soluble in the simple acids and the unchanged oil. A practically

complete separation of the hydroxy acids from the oxidized mixture may be obtained by adding to the oxidized mixture fresh hydrocarbon distillate and separating the hydroxy acids from the unoxidized oil and simple acids by gravity.

In either case, whether the hydrocarbon is oxidized to form the simple acids or the hydroxy acids, both types of acids are formed. To recover the two kinds of acids separately the oxidized mixture is first subjected to gravity separation to recover the hydroxy acids and is then washed with alkali to recover the simple acids and the residual hydrocarbon is returned to the oxidizing apparatus. This procedure of course accomplishes only a crude separation and is effective only when the oxidation is carried to the point at which the hydroxy acids are the principal product. When the hydrocarbon is only oxidized to the extent of about 20 per cent the gravity separation is omitted and the whole of the acid content recovered by treatment with alkali. The acids are then recovered from the alkali by means of acid and the hydroxy acids are separated by treating the mixture with strong sulfuric acid which dissolves the hydroxy acids and at the same time removes colored impurities from the undissolved simple acids.

I have found that in starting the process with new apparatus it is desirable to add to the batch of hydrocarbon to be oxidized a catalytic agent or oxygen carrier. The known hydrocarbon-soluble organic salts or compounds of manganese iron and copper have been found to be suitable. The addition of such compounds promotes the initial oxidation of the hydrocarbon. After the apparatus has been used for a time the surfaces in contact with the hydrocarbon ap-

parently develop catalytic properties and the use of added catalytic agents is unnecessary, the reaction rate being substantially the same without the addition of a catalytic agent as when the catalytic agent is used.

I claim:

1. Process which comprises agitating a normally liquid hydrocarbon containing an aliphatic chain, in liquid phase, in contact with an oxidizing gas at a temperature of at least about 100° C. and at a pressure of from about 100 pounds to about 320 pounds per square inch.

2. Process which comprises agitating a normally liquid petroleum hydrocarbon in liquid phase in contact with a stream of air at a temperature of from about 120° C. to about 130° C. and at a pressure of about 150-180 pounds per square inch.

3. Process as defined in claim 2, in which the stream of air is supplied to and removed from contact with the hydrocarbon at such a rate that about 40 per cent of its oxygen content is consumed.

4. Process which comprises agitating at a temperature above about 120° C. and at a pressure of about 150-180 pounds per square inch a normally liquid petroleum hydrocarbon in liquid phase, in the absence of alkalies, in contact with a stream of air supplied to and removed from contact with the hydrocarbon at such a rate that about 40 per cent of the oxygen content of the air is consumed, separating the resulting hydroxy carboxylic acids from the liquid, and subsequently treating the liquid with an aqueous solution of a caustic alkali.

In testimony whereof, I affix my signature.

ARTHUR W. BURWELL.