Sept. 30, 1941. E. W. LUSTER 2,257,177

POLYMERIZATION BY MEANS OF A HIGH FREQUENCY ELECTRIC DISCHARGE

Filed July 17, 1937 3 Sheets-Sheet 1

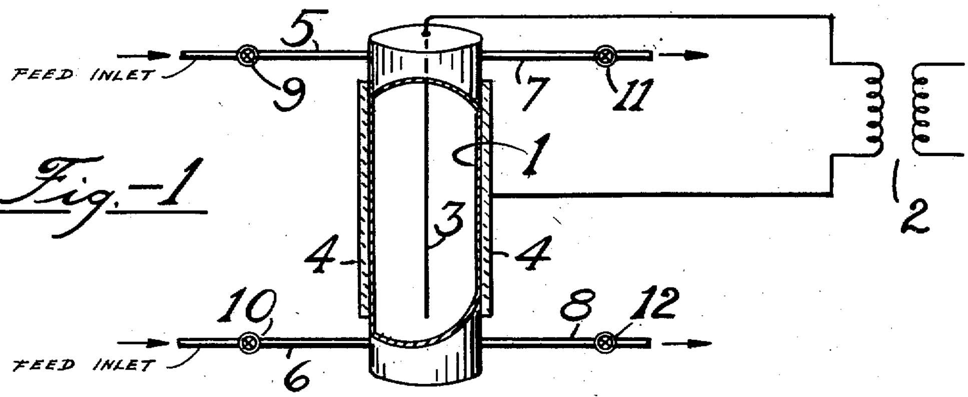

Fig.-1

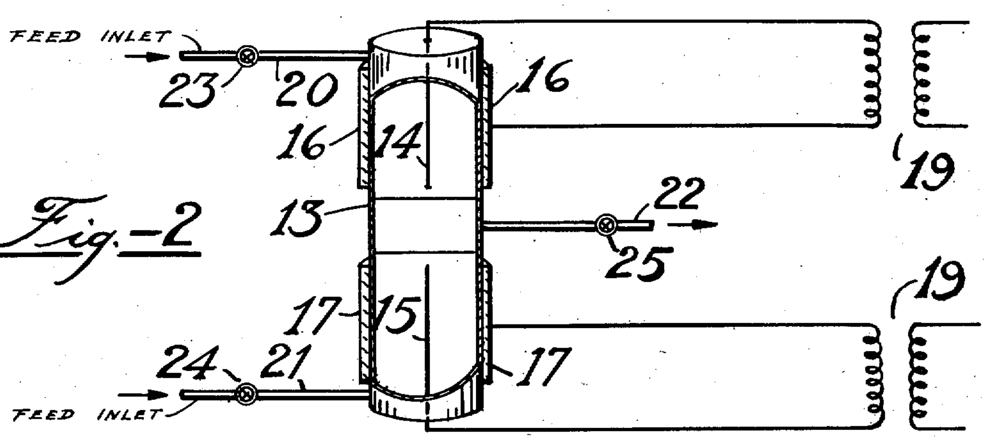

Fig.-2

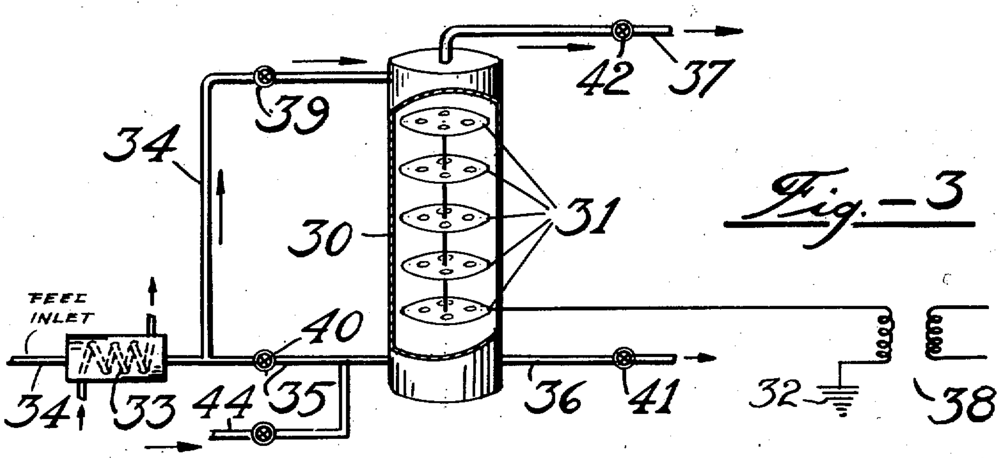

Fig.-3

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POLYMERIZATION BY MEANS OF A HIGH FREQUENCY ELECTRIC DISCHARGE

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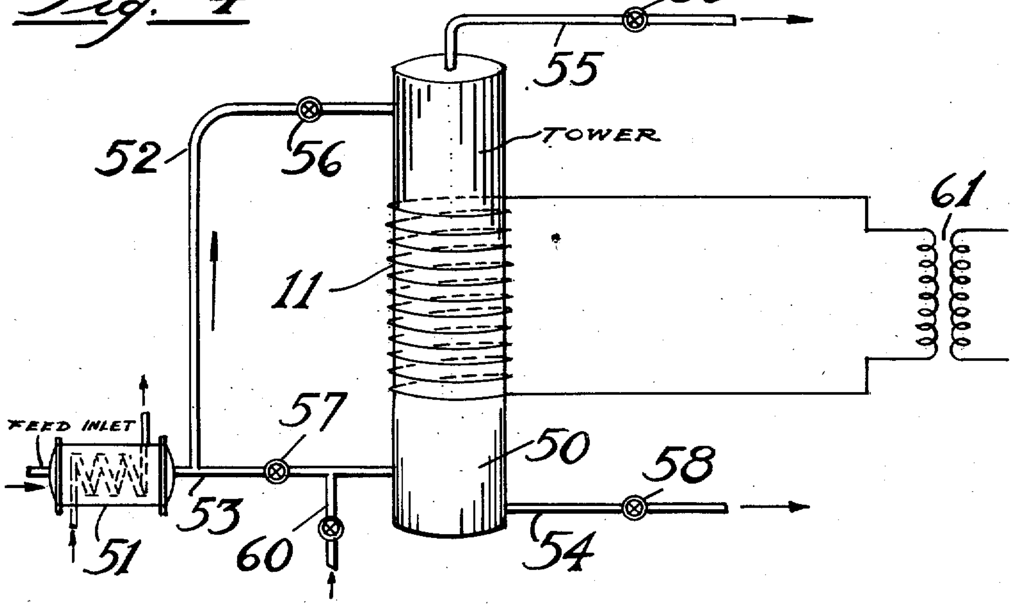
Fig.-4



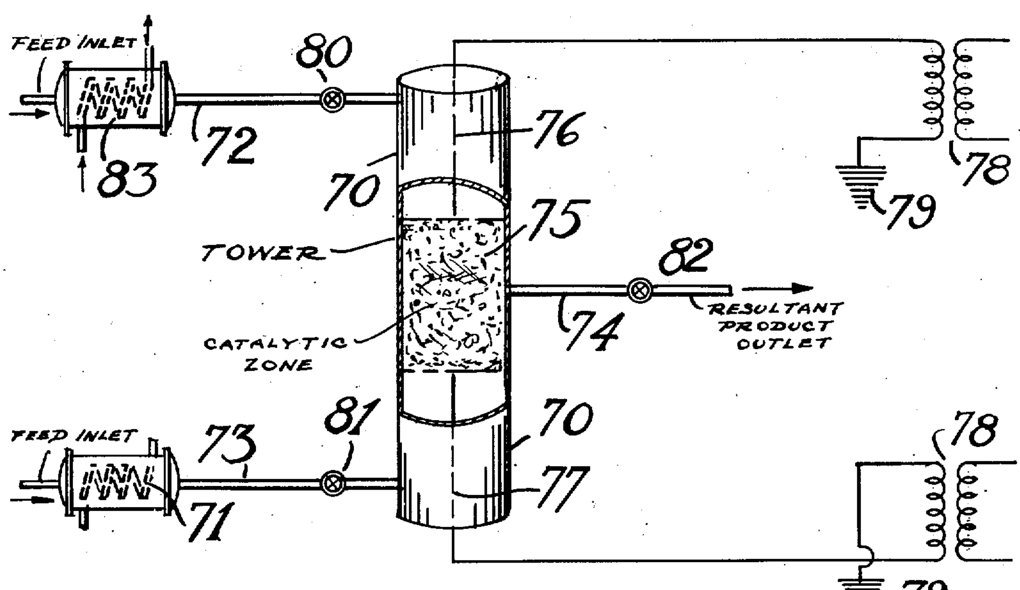


Fig.-5

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POLYMERIZATION BY MEANS OF A HIGH FREQUENCY ELECTRIC DISCHARGE

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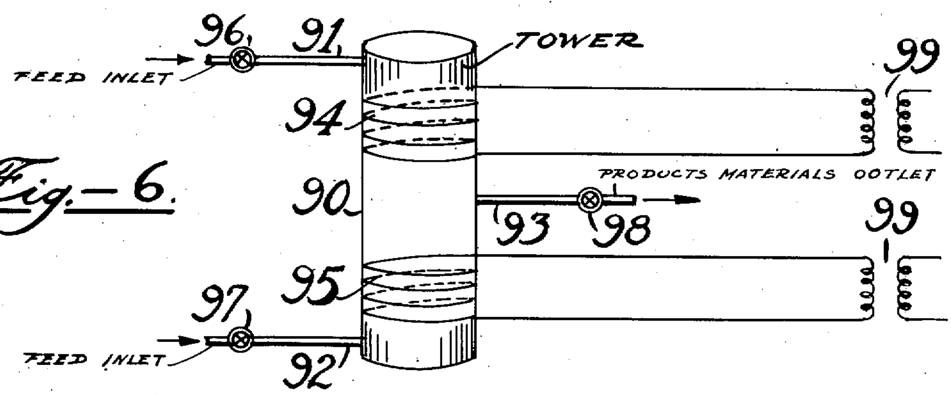

Fig.-6.

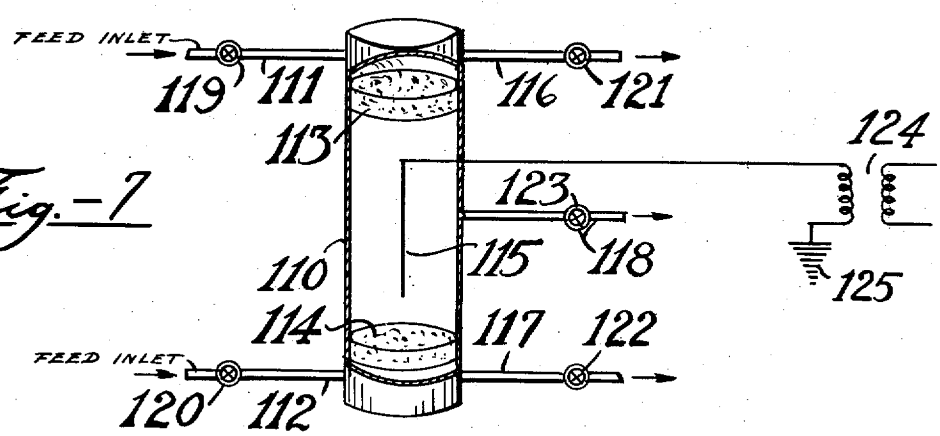

Fig.-7

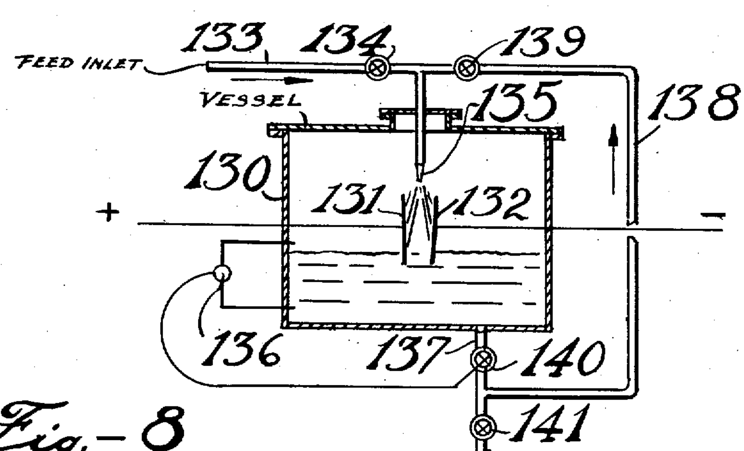

Fig.-8

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Patented Sept. 30, 1941 2,257,177

UNITED STATES PATENT OFFICE

2,257,177

POLYMERIZATION BY MEANS OF A HIGH FREQUENCY ELECTRIC DISCHARGE

Eric W. Luster, Westfield, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

Application July 17, 1937, Serial No. 154,324

3 Claims. (Cl. 204—168)

This invention relates to the process of conducting a chemical reaction by means of a high frequency electric discharge. It further relates to the process of conducting chemical reactions at frequencies at which one electrode or no electrodes but a ring coil is employed. It also relates to the process of conducting a chemical reaction of sufficiently high frequencies and low voltages whereby the necessity for an insulating material is dispensed with. It particularly relates to the process of conducting a chemical reaction by means of high frequencies in the range above about 1 megacycle, especially in the range above 600 megacycles. The present invention further relates to the art of subjecting organic material to the effect of a high frequency discharge and particularly to the art of subjecting these materials, especially petroleum hydrocarbons, to the effect of a high frequency electric discharge and preferably to high frequency glow discharges.

The process of subjecting materials to the effect of the electric or glow discharge, commonly known as voltolization, is old. The usual process involves treatment of the material by means of two electrodes spaced relatively close together and at frequencies below 10,000 cycles. This known process of voltolization is not to be confused with the present invention which is concerned with frequencies of the magnitude in which the electrons are apparently withdrawn to the same electrode since the polarity changes before the electrons pass from the zone of influence. It is within the concept of the present invention to have the frequencies of the electric discharge approach electronic frequencies.

I have discovered that if frequencies above 1 megacycle, preferably in the range above 600 megacycles, are used, startling and unexpected advantages result therefrom. At these frequencies I have found; that it is possible to produce dehydrogenation, polymerization or additive or chemical reactions; that these reactions may be secured by means of one electrode, or no electrode if a ring coil be used; that lower voltages may be used, thereby lessening the operating and initial cost of the apparatus in that the strength of the dielectrics may be lessened or completely eliminated; that the operation will be more uniform since a possibility of sparkovers will be considerably lessened resulting in a better quality of product; that a catalytic mass may be made to glow in the electromagnetic field or to actually act as one electrode, thus greatly adding to the efficiency of the operation; that although a vacuum is generally preferred, in some cases satisfactory results can be secured at atmospheric pressure.

The attached drawings serve to illustrate some of the modifications of the present invention.

Figure 1 is a diagrammatic side view of a two electrode apparatus.

Figure 2 is a side view of a two electrode apparatus in which the feed components may pass through separate electromagnetic fields before reacting.

Figure 3 is a diagrammatic side view of a one electrode apparatus in which the electrode may be a series of plates used for fractionation or distribution of the materials being treated.

Figure 4 is a side view of an apparatus in which no electrode is used and in which the electromagnetic field is set up by means of a ring coil. The tower may contain suitable fractionating or distributing plates or a catalyst.

Figure 5 is a side view of an apparatus having two distinct electromagnetic fields, each of which is set up by means of one electrode.

Figure 6 is a side view of an electrodeless apparatus having two distinct electromagnetic fields set up by separate ring coils.

Figure 7 is a side view of an apparatus having one electrode and two separate catalytic masses through which the feed materials pass before entering the high frequency electromagnetic zone.

Figure 8 is a side view of a two electrode high frequency apparatus in which a dielectric between the electrodes is not employed.

Referring particularly to Figure 1, in which 1 designates an atmospheric pressure or evacuated vessel or tower into which either vapor or liquid feed materials may be fed through either feed lines 5 or 6 and withdrawn through either take-off lines 7 and 8 after passing through the electromagnetic field set up by the electrodes 3 and 4. Tower 1 may be dielectric or may be suitably insulated from the electrodes. The tower may also act as electrode 4 if adequately insulated from electrode 3. Control valves 9, 10, 11 and 12 of the respective feed and take-off lines and a source of high frequency alternating current 2 are shown. The vessel or tower may contain suitable fractionating or distribution plates or be packed with a suitable catalyst. The plates or catalytic mass, if satisfactory, may serve as electrode 3.

In Figure 2, 13 designates an atmospheric pressure or evacuated tower or vessel into which either liquid or vapor feed materials may be fed through either feed lines 20 and 21 and be withdrawn through take-off line 22, after passing through the electromagnetic fields set up by electrodes 14 and 16 and electrodes 15 and 17 respectively. Tower 13 is suitably insulated from the electrodes or may be of dielectric material. Control valves 23, 24 and 25 are shown on the respective feed and take-off lines. High frequency alternating current source 19 is also shown. Said type of apparatus may be either in a vertical or horizontal position and may be packed or contain catalytic materials or suitable fractionating or distributing plates which may act as electrodes 14 and 15.

In Figure 3, 30 represents an atmospheric pressure or evacuated tower or vessel into which either liquid or vapor feed materials may be fed through either feed line 34 or 35 and withdrawn by means of either take-off lines 36 or 37, after passing through the electromagnetic field set up by means of one electrode, which in the particular case shown is a series of perforated plates 31. Tower 30 is suitably insulated from electrode 31 or may be of dielectric material. Control valves 39, 40, 41 and 42 are shown on the respective feed and take-off lines. A preheating coil, 33, in which feed materials may be preheated, a source of high frequency alternating current, 38, and a ground, 32, of the electrode circuit are also shown. Coil springs or catalytic masses may serve as electrode 31. The plates of electrode 31 are perforated to secure distribution of the feed materials passing through the tower, but other means of distribution may be used. The apparatus, as for example in Figure 3, might also be operated in a manner by feeding liquid in by means of feed line 34 and introducing a vapor or gas by means of feed lines 35 and 44, thereby allowing the liquid to pass downwardly through the tower contacting the upflowing gases in the electromagnetic field set up by the electrode distributing plates. The products made are then removed by means of take-off lines 36 and 37. The electrode may be a single rod or catalytic mass rather than the plates as shown.

In Figure 4 the atmospheric pressure or evacuated tower or vessel, 50, is fed with either vapor or liquid feed materials by means of either feed lines 52 or 53 and the products removed by means of take-off lines 54 or 55 after passing through the electromagnetic field set up by means of ring coil 11. Tower 50 is of dielectric material if the ring coil is on the outer surface of vessel 50, as shown in Figure 4. The ring coil 11 may be placed within tower 50, in which case the tower may be of dielectric material or suitably insulated from the ring coil 11. Tower 50 and ring coil 11 may represent one tube element of a tube bundle, in which the tubes are in parallel and are similarly wound with the ring coil. Thus it is within the scope of the present invention to employ a multiplicity of tubes having diameters preferably from 1 to 3 inches, each tube having its own ring coil and the treating tower built somewhat like a tubular heat exchanger. Control valves 56, 57, 58 and 59 on the respective feed and take-off lines are shown. A source of high frequency alternating current, 61, and a furnace coil, 51, in which the feed materials may be preheated are also shown. The evacuated tower may contain fractionating or distributing plates or a catalytic mass or contain a catalytic mass which may be caused to glow in the electromagnetic field.

In Figure 5 the atmospheric pressure or evacuated tower or vessel 70 may be fed with either liquid or vapor and may be introduced by means of either feed lines 72 or 73. The respective feed materials pass first through the electro-magnetic zone set up by electrodes 76 and 77 and then contact each other in the catalytic zone 75. The resultant product is withdrawn through take-off line 74. Tower 70 may be suitably insulated from the electrodes or may be of dielectric material. Control valves 80, 81 and 82 on the respective feed and take-off lines and a source of high frequency alternating current, 78, are shown.

In Figure 6, 90 represents an atmospheric pressure or evacuated tower or vessel into which materials are fed by means of either feed lines 91 or 92. The feed materials may be either liquid or vapor, and pass through separate electromagnetic fields set up by separate ring coils 94 and 95 respectively, before contacting each other. The product materials are withdrawn through take-off line 93. Tower 90 is of dielectric material if the ring coil be placed on the outer surface. If the ring coil be placed within tower 90, the tower may be of dielectric material or may be suitably insulated from the ring coils. Tower 90 may be of a small diameter and represent one tube element of a tube bundle. The apparatus would then be somewhat similar to a tubular heat exchanger. Cooling or heating means could be circulated on the outside surface of the tubes. Control valves 96, 97 and 98 on the respective feed and take-off lines and a source of high frequency alternating current, 99, are shown.

In Figure 7, 110 represents an atmospheric pressure or evacuated tower into which either liquid or vapor materials may be fed through feed lines 111 or 112. The feed materials first pass through separate catalytic masses 113 and 114 before coming into contact with each other in the electromagnetic field set up by the single electrode 115. The products may be withdrawn by means of take-off lines 116, 117 or 118. Tower 110 may be of dielectric material or be suitably insulated from the electrode. Control valves 119, 120, 121, 122 and 123 on the respective feed and take-off lines, a source of high frequency alternating current, 124, and the ground connection, 125, of the electrode circuit, are indicated.

In Figure 8, 130 represents an atmospheric pressure or evacuated vessel. Feed materials may be fed through feed line 133, controlled by valve 134, and sprayed between the electrodes 131 and 132 by means of nozzle 135. The electrodes 131 and 132 may dip into a liquid level maintained by liquid level controller 136. The treated materials may be withdrawn through take-off line 137 or re-cycled by means of line 138. Control valves 139, 140 and 141 on the respective lines are shown. This apparatus may be so modified that nozzle 135 will feed upwardly through the electromagnetic field, thereby allowing the treatment of gases or vapors. The tower or vessel may be of any suitable material or composition and may be dielectric or may be suitably insulated.

The invention consists in conducting a chemical reaction by holding or passing materials through an electromagnetic field produced by a high frequency alternating current in various ways, some examples of which have been given. The chemical reaction may be conducted with organic or inorganic materials under wide conditions of temperature and pressure. Organic material, as for example substances from the classes of aliphatic, aromatic or cyclic hydrocarbons, alcohols, aldehydes, ketones, acids, esters and the like may be used as well as halogen, nitrogen, sulfur or other substitution products and derivatives thereof. Preferably, materials selected as feed stocks are petroleum hydrocarbons. The above materials may be treated for the purpose of producing dehydrogenation, polymerization, additive compounds or chemical reaction.

The apparatus consists essentially of an atmospheric pressure or evacuated tube or chamber, or equivalent thereof, located in an electromagnetic field of either one or two electrodes, or in the electromagnetic field of a ring coil connected to a high frequency alternating current source. The tube or chamber may be at atmospheric pressure or may be evacuated to a pressure of about .001 mm. or lower absolute. It is preferable, however, to operate in a vessel evacuated to a pressure of about 10 to 100 mm. of mercury, preferably evacuated to below about 40 mm. particularly at a pressure of about 20 mm. of mercury. At these preferred operating ranges optimum results are secured in regard to current, density and resulting chemical reaction.

The high frequency alternating current is preferably secured by means of a vacuum tube high frequency generator circuit suitably connected to said electrodes or ring coil. However, any other method of securing high frequencies would be satisfactory.

The electromagnetic field may be produced by means of two electrodes connected to a source of high frequency current and the material being treated may be passed in various ways through the field between said electrodes, as shown in Figures 1 and 2. However, the preferred method is to have one electrode, or no electrode but a ring coil, producing the electromagnetic field, as shown in Figures 3, 4, and 5. When using one electrode, one end of the electrode circuit is grounded. The frequencies with which this application is concerned are those above 1 megacycle, and particularly those frequencies above 600 megacycles. A very desirable method of this invention is to use one electrode or a ring coil at the very high frequencies, thus producing a glow discharge. The evacuated tube or chamber may contain catalytic materials which may be caused to glow in the electromagnetic field set up by a ring coil, as in Figure 4. Certain catalytic materials may act as the electrode in the atmospheric pressure or evacuated tube or chamber.

The feed material may be either in the vapor or liquid state, and may be treated in the various ways as shown in the drawings. The flow may be either up or down, with either liquid or vapor. A stream may enter at each end taking off the product from the center zone, as shown in Figures 2 and 5. A catalyst may be used to activate the material and may be used in various modifications as, for instance, the catalyst may activate each of the two components before, during or after the feed materials are subjected to the effect of the electric discharge prior to blending for reaction. As previously mentioned, certain catalytic masses may serve as electrodes. Vapor or liquid feed materials may be treated separately in respective electromagnetic fields, thereafter contacting each other, as for example as shown in Figure 6. Suitable mixing or distributing plates or means may be employed. Catalysts may also be employed at any stage of the process. Feed materials may be introduced in either a liquid or vapor state and contact respective catalytic masses, thereafter contacting each other in an electromagnetic field set up by one electrode, as shown, for example, in Figure 7. Liquid feed material may flow downwardly through the tower, contacting the upflowing gases, and the respective products removed by means of lines **116** and **117**. If the feed materials are both in the vapor state, the resulting product may be removed, for instance, by line **118**. Distributing plates, or contacting masses may be employed.

Materials may be treated on a chemical reaction conducted in an electromagnetic field set up by means of two electrodes in which a dielectric material is not employed, as for example as shown in Figure 8. The design may vary widely, as also the distance between the electrodes and the area of the electrodes. The electrodes may be of the plate, multiple plate or cylindrical design. Vapor or liquid may be fed either downwardly, upwardly or horizontally.

By conducting chemical reactions and treating organic substances in this manner, many advantages and improvements are obtained. At these high frequencies relatively low voltage may be used. Thus this simplifies and lessens the cost of the mechanical construction of the equipment used in treating materials with electric discharge. The possibility of sparkover is considerably lessened and a finer control of the operation can be maintained, resulting in higher grade products with one electrode or a ring coil. When an electromagnetic field is produced by means of one electrode or a ring coil or a catalytic mass acting as one electrode, the cost of the equipment is considerably lessened and the problem of securing satisfactory operation is materially decreased. The advantages over the present type of plate electrode are tremendous in that greater throughputs and yields can be obtained, thereby putting the process on a sounder commercial basis.

This invention is not to be limited by any specific examples or descriptions but only by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

I claim:

1. A process of polymerizing petroleum hydrocarbons which comprises subjecting said hydrocarbons in liquid state at a pressure in the range of 0.001 to 100 mm. of mercury absolute to the action of a high frequency glow discharge produced by means of a single electrical conducting electrode carrying an alternating electric current having a frequency above 1 megacycle, and maintaining the glow discharge under a pressure sufficiently low and with a sufficiently high frequency to sustain said glow discharge from said electrode independently of discharges from any other conducting electrode until said hydrocarbons are substantially polymerized.

2. A process as described in claim 1, in which said glow discharge has a frequency above 600 megacycles and oscillates directly to and from and in contact with said conducting electrode by which it is produced.

3. A process of polymerizing petroleum hydrocarbons which comprises subjecting said hydrocarbons in liquid state at pressures from 10 to 40 mm. of mercury absolute to the action of a high frequency electrodeless glow discharge, and maintaining said glow discharge under sufficiently low pressure and with sufficiently high frequency above 1 megacycle so that the glow discharge is sustained until said hydrocarbons are substantially polymerized.

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