Industry Canada Industrie Canada

Canada

strategis.gc.ca

Strategis Index:

CIPO OPIC

CIPO HOME

The Canadian Intellectual Property Office

Canadian Patents Database

12/19/2001 - 13:23:28

(12) **Patent:**

(11) **CA 535879**

(54) PRODUCTION OF FUEL OR SYNTHESIS GAS

(54) PRODUCTION DE COMBUSTIBLE OU DE GAZ DE SYNTHESE

(72) (Country):	**NORMAN H. WILLIAMS** (Not Available)
(73) (Country):	**HUMPHREYS AND GLASGOW LIMITED**
(71) (Country):	
(74)	
(45)	**Jan. 15, 1957**
(22)	
(43)	
(52)	**48/27**
(51)	**N/A**
	No
(30)	**None**
	N/A
	Unknown

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
- Disclosures Image
- Drawings Image

This invention relates to the production of combustible gases from tars, hydrocarbon oils or gases, or the like, by reacting them in the presence of a catalyst with oxidising gases such as steam and carbon dioxide or gases containing free oxygen or mixtures of these gases.

Examples of such processes are the production of fuel gas or synthesis gas from hydrocarbon oils by reaction with steam or steam and carbon dioxide. In some such processes the addition of some air to the steam or carbon dioxide is permissible and serves to diminish carbon deposition.

It is known to conduct such processes either cyclically or in a continuous manner. In processes of the cyclic type, the production of gas is alternated with the re-heating of the bed of catalyst in the reaction chamber. In processes of the continuous type, heat may be imparted to the catalyst by heating the exterior of the vessel or tubes containing it or, alternatively, the catalyst may be removed from the reaction chamber and re-heated elsewhere, the quantity of catalyst in the reaction vessel being maintained by the supply to the reaction vessel of an equivalent amount of fresh or re-heated catalyst. In processes of the latter type the catalyst is usually heated either by direct contact with hot combustion products or by the combustion of carbon, oil or the like on or around the catalyst, and it is with processes of this type that the present invention is concerned.

Many catalysts known to be suitable for promoting reaction between hydrocarbon vapours or gases and steam or carbon dioxide are composed of or contain constituents, of which iron or nickel in the form of metal oxide are well-known

and common examples, and which constituents are readily reducible or oxidisable and in many cases form more than one oxide. Accordingly, while in contact with the reactants during the production of the combustible gas these catalysts or catalyst constituents are converted to the metal or to lower oxides or mixtures thereof.

During the said production of the combustible gas, carbon is normally deposited upon the catalyst and the catalyst is also cooled by the endothermic nature of the reactions with steam and/or carbon dioxide. It is therefore necessary both to re-heat the catalyst and to remove carbon from it. These two results are usually achieved simultaneously by burning-off the deposited carbon with air, additional heat being supplied, if necessary, by combustion of oil, tar or the like.

The air supplied for this combustion and heating process also converts the catalyst to a more oxidised state as also, in many cases, does the carbon dioxide resulting from burning of the carbon deposits. This is undesirable because, the catalyst, when next used in the production of combustible gas, is again reduced by reaction with the combustible gas or the oil vapours, with formation of carbon dioxide and/or water. This reduces the yield of desired products and also contaminates the product gas with carbon dioxide. It is an object of the present invention to provide a process whereby catalysts which are readily oxidised and reduced at the temperatures prevailing in the process may be used with minimum oxidation of the catalyst while it is being heated and, consequently, minimum production of carbon dioxide and water from the process reactants during the use of the catalyst for gas production.

In processes of the type in which an oxidisable catalyst is used in a fixed bed through which are passed alternately hydrocarbon gas or vapours together with steam for reaction, and air for combustion of carbon deposited thereon and for heating the catalyst, the carbon deposits are burnt off first at that end of the column of catalyst at which the air enters and air for combustion of the remaining carbon has to pass over catalyst already freed from carbon. In doing so it oxidises this catalyst. There is some improvement if the air is passed first in one direction and then in the other but in order to burn off the carbon in the central region of the bed it is still impossible to avoid oxidising the catalyst at the ends of the bed.

If the catalyst is used for the desired catalytic reaction in a fluidised reaction bed and then treated with air for combustion of carbon in another fluidised bed before being returned to the first reaction bed, oxidation of the catalyst in the carbon-burning bed occurs because, by the nature of a fluidised bed, individual catalyst particles are not removed from the bed as soon as the carbon deposits have been burnt from them but generally remain in the bed for a longer time and become oxidised.

Within the temperature range suitable for the catalytic reaction of steam and/or carbon dioxide with hydrocarbon gas and/or vapours, viz: about 600°C. to 1,100°C., the rate of reaction of oxygen with the carbon deposits is much faster than its rate of reaction with the catalyst constituents and very much faster than the rate of reaction with these constituents of the carbon dioxide formed by combustion of the carbon deposits.

In carrying out our invention we provide a vessel in

which the gas-producing reactions between hydrocardon material and steam and/or carbon dioxide take place in a solid bed or a fluidised bed of catalyst and we continually remove portions of the catalyst from this bed for re-heating and combustion of carbon deposits.

According to the present invention there is provided a process for the production of combustible gases by reaction of a hydrocarbon material in a reaction zone with an oxidising gas in the presence of a readily oxidised and reduced catalyst which comprises withdrawing hot used catalyst from the reaction zone, passing the used catalyst through a regenerating zone together with a gas stream containing molecular oxygen in an amount not substantially exceeding that required for combustion of carbon deposits on the used catalyst, the said used catalyst together with the said gas containing molecular oxygen being passed through the regenerating zone in the same direction and at such a rate that the contact time between said catalyst and said gas in said regenerating zone is not substantially greater than the time required for burning-off said carbon deposits, and subsequently recycling treated catalyst to the reaction vessel.

The catalyst may pass through the catalyst regenerating zone e.g. a heating vessel or pipe, in which it is heated and in which carbon deposits are burned from it either as a moving bed or column of particles or pieces resting one upon another or as a suspension in

the air or as a fluidised stream but in the latter case the rate of flow through the vessel or pipe and the dimensions of the pipe must be such that the catalyst passes through it as a flowing stream.

By using an appropriately larger quantity of catalyst in the reaction chamber for steam and hydrocarbons to make up for the loss of active catalyst surface, the conditions in the carbon-burning pipe or vessel may be adjusted so that some carbon still remains in the catalyst when it leaves this vessel provided that in its subsequent use in the reaction vessel the amount of residual carbon thus remaining does not lead to an undesired amount of thermal cracking, which is catalysed by carbon. When it is permissible to leave some unburnt carbon in the catalyst leaving the burning-off vessel, oxidation of the catalyst itself in this vessel can more easily be reduced to a minimum.

By the process of our invention we are able to use catalysts of an oxidisable character, many of which materials are strongly active in promoting the desired reactions between hydrocarbon gases or vapours and steam without the disadvantage of converting part of the hydrocarbon material into carbon dioxide and

water by the reactions involved in reducing the catalyst from a higher to a lower state of oxidation.

When applying the process of our invention the waste gases leave the vessel in which the carbon deposits are burnt from the catalyst at substantially the temperature to which the catalyst is heated. The sensible heat of these waste gases may be recovered in regenerators or other devices for transferring heat from one fluid to another (hereinafter referred to as heat exchangers) and thus be used to heat the air for carbon burning and/or steam for reaction or it may be recovered in a waste heat boiler or partly in one way and partly in the other, depending on the extent of the carbon deposits in relation to the heat requirements of the process and on the availability or otherwise of steam for the reaction and on various other considerations.

It is understood that where the heat derived from combustion of the carbon deposits is inadequate for the heat requirements of the process it may be supplemented by combustion of oil, tar or the like. In this case it is convenient to combust the oil in the air supplied for burning off the carbon deposits before this air is led into the catalyst column for combusting said deposits. Thus the oil is burned in an excess of air and the resulting hot mixture of air and combustion products is used for burning carbon from the catalyst.

The following is a description of two embodiments of apparatus in which the process of the present invention may be carried into effect, the description being with reference to the following drawings in which:

Figure 1 is a diagrammatic representation of one embodiment of apparatus and

Figure 2 is a diagrammatic representation of the alternative form of apparatus.

Referring to Figure 1 there is a reaction vessel 1 for containing the catalyst having steam inlets 2 located near the inverted conical base of the reaction vessel 1 and inlets 3 for feeding oil into the reaction vessel at a point above the point of steam feed. At the top of the reaction vessel 1 is an off-take pipe 4 for the reaction products.

At the bottom of the reaction vessel 1 there is a rotary valve 6 for withdrawing catalyst therefrom, fresh catalyst being fed into the reaction vessel through the feed pipe 5 at the top thereof. Communicating with pipe 5 is a valved inlet 7 for the supply of steam to seal the pipe 5 against passage therethrough of gases from either the reaction vessel 1 or the regenerating vessel 11.

The rotary valve 6 communicates with a conduit 8 which leads to the bottom of a mechanical lift 9 in which a bucket elevator operates in a closed circuit to lift the used catalyst withdrawn from the bottom of the reaction vessel 1 and feed it up to a second rotary valve 10 which passes the used catalyst into a regenerating vessel 11 disposed vertically above the reaction vessel 1 and communicating therewith through the feed pipe 5 above referred to.

Near the base of the regenerating vessel 11, above the constriction forming feed pipe 5, there is a gas-collecting annulus 111 constituted by an abrupt increase in the interval diameter of the vessel 11. Owing to the angle of repose of the solids this annulus remains clear of catalyst as it descends into the wider portion of vessel 11. An offtake 12 is provided for

leading off the waste gases that collect in the annulus 111.

Connected to the top of regenerating vessel 11 is a pre-combustion chamber 13 into which air is fed through pipe 14 from a blower 15 either through a pipe 16 or through a heat exchanger 17 in which the air is pre-heated by heat exchange with the waste gases taken off from the vessel 11 through the offtake 12. If desired, heating oil may be introduced into the pre-combustion chamber 13 through the valved inlet 18 in those circumstances where the amount of carbon deposited on the catalyst is insufficient, when combusted by the air, to generate sufficient heat for effective reheating of the regenerated catalyst in the vessel 11.

The heat in the waste gases taken from the vessel 11 through the offtake 12 may be employed as above indicated for preheating the air in the heat exchanger 17 or it may be passed through the waste-heat boiler 19 for the raising of steam or, alternatively, the waste gases may be passed through a second heat exchanger 20 for preheating the steam being fed into the reaction vessel 1 through the inlets 2.

The various pipes and inlets are provided with appropriate control valves generally indicated in the diagrammatic drawing but not specifically referred to above.

In the operation of the process, the steam and oil are fed into the reaction vessel 1 through the appropriate inlets 2 and 3, the body of catalyst in the reaction vessel being previously heated to an appropriate temperature. The used catalyst is withdrawn through the rotary valve 6 and conveyed by the bucket elevator 9 through the rotary valve 10 to the catalyst regenerating vessel 11 through which air is passed, the air, if desired, being preheated in the heat

exchanger 17 and, if necessary, further heated by combustion of oil in the pre-combustion chamber 13 by means of oil fed in through inlet 18 and ignited in the chamber 13. The rate of circulation of the catalyst is such that the residence time of the used catalyst in the vessel 11 and the rate of air flow therethrough is such that the amount of oxygen consumed is not substantially more than sufficient to combust the carbon deposits on the catalyst by the time it reaches the feed pipe 5 for entry back into the reaction vessel 1. By controlling the rate of movement of the used catalyst through the vessel 11 and by controlling the amount of the co-flowing stream of air and its preheating, regeneration is effected of a moving body of catalyst. Combustion of carbon deposits thereon, therefore, takes place uniformly and can be controlled so that it is not completed to the desired extent until the catalyst is about to re-enter the reaction vessel thereby making it possible to avoid undesirable oxidation of a readily oxidisable catalyst, for instance a catalyst containing iron or nickel.

In the alternative apparatus diagrammatically illustrated in Figure 2, there is a cylindrical reactor 21 provided with a pipe 22 for feeding steam to an injector 222 to which regenerated catalyst is fed and in which it is fluidised and fed to the base of the reactor and inlets 23 for feeding in of oil. The reactor may be provided with additional inlets 24 and 25 for feeding in additional oil and steam directly at different levels in the reactor if required.

At the top of the reactor 21 is an offtake pipe 26 leading to a cyclone separator 27 from the top of which the offtake 28 leads away the gaseous reaction products.

The catalyst particles separate out from the gas stream in the cyclone separator 27 and pass downwardly through the pipe 29 into an uprising regenerating vessel 30 into which air is injected from pipe 31 and, if desired, introduced also at inlets 32 so as to fluidise the catalyst and lift it upwardly through the vessel 30. Combustion of carbon deposits on the used catalyst is thus effected with a co-flowing stream of air whilst it is in the vessel 30.

The air supplied to pipe 31 and inlets 32 is forced by blower 33 either through a heat exchanger 34 or through a by-pass pipe 35, the air, after having regenerated the catalyst in the vessel 30, being separated from the catalyst in the cyclone separator 36 from which regenerated catalyst passes downwardly via the connecting pipe 37 to re-enter the reactor 21 via the injector 222, and the hot waste gases being withdrawn through the pipe 38 via the heat exchanger 34. The hot waste gases may, if desired, be passed through the waste heat boiler 39 for raising steam or may be passed through a pipe 40 to a second heat exchanger 41 for pre-heating of the steam being fed through pipe 22.

In the operation of the apparatus described with reference to Figure 2, the general procedure is the same as that described in relation to Figure 1 save for the differences in operation arising from the use of a fluidised catalyst as distinct from the packed bed of catalyst employed in Figure 1. Thus, the steam entering the reactor 21 through the pipe 22 fluidises the regenerated catalyst passing down pipe 37 in the injector 222 and the reaction with oil takes place in the reactor 21 in contact with a fluidised catalyst, the used catalyst being separated out subsequently in the

cyclone separator 27 and the conditions for carbon burning in the regenerating vessel 30 being such that the desired extent of combustion of the carbon on the catalyst is not substantially completed before it passes back to the reactor 21 via the connecting pipe 37.

Thus, in the process carried out in the apparatus described with reference to Figure 2, an undesirable extent of oxidation of the catalyst is avoided in a similar way to that described with reference to Figure 1.

It will be appreciated that the foregoing description with reference to the two figures of the drawings is not exhaustive of the various types of apparatus and process which are embraced by the invention and the description is intended to be illustrative only of two possible ways of carrying into effect the process of the invention relating to the regeneration of the catalyst whilst substantially avoiding its oxidation.

I CLAIM:-

1. A process for the production of combustile gases by the reaction of a hydrocarbon material in a reaction zone with an oxidising gas in the presence of a readily oxidised and reduced catalyst which process comprises withdrawing hot used catalyst bearing deposited carbon from the reaction zone, passing the said used catalyst through a regenerating zone together with a gas stream containing molecular oxygen in an amount not substantially exceeding that required for combustion of the said deposited carbon on the used catalyst, the said used catalyst together with the said gas containing molecular oxygen being passed through the regenerating zone in the same direction and at such a rate that the contact time between said used catalyst and said gas in said regenerating zone is not substantially greater than the time required for combustion of said deposited carbon and subsequently recycling catalyst so regenerated to the reaction zone.

2. A process according to claim 1 wherein the spent catalyst is passed through said regenerating zone in the form of a moving column wherein the pieces of catalyst rest one upon another.

3. A process according to claim 1 wherein the used catalyst is passed through said regenerating zone in the form of a suspension in said gas stream.

4. A process according to claim 1 wherein the used catalyst is passed through said regenerating zone in the form of a fluidised stream.

5. A process according to claim 1 wherein the conditions in the regenerating zone are so adjusted that only a partial combustion of the said deposited carbon is effected.

6. A process according to claim 1 wherein the hot gases from the regenerating zone are passed through a heat exchanger for the recovery of sensible heat therefrom.

7. A process according to claim 6 wherein the sensible heat recovered in said heat-exchanger is employed for preheating the gas for regeneration of the used catalyst.

8. A process according to claim 1 wherein sensible heat in hot gases from the regenerating zone is employed for raising steam in a waste-heat boiler.

9. A process according to claim 6 wherein the sensible heat recovered in said heat-exchanger is employed for preheating oxidising gas prior to its introduction into the reaction zone.

10. A process according to claim 1 wherein a combustible material other than the carbon deposits on used catalyst is burnt in the gas stream in the regenerating zone to provide additional heat for regeneration of the said used catalyst.

11. A process according to claim 10 wherein the said combustible material is added to the gas stream prior to its contact with catalyst in the regenerating zone.

12. A continuous process for the production of combustible gases by reaction of a hydrocarbon material in a reaction vessel with an oxidising gas in the presence of a readily oxidised and reduced catalyst which comprises continually withdrawing hot used catalyst from the reaction vessel, passing the used catalyst through a pipe together with a gas stream containing molecular oxygen in an amount not substantially exceeding that required for combustion of carbon deposits on the used catalyst, the said used catalyst together with the said gas containing molecular oxygen being passed through the pipe in the same direction and at such a rate that the contact time between said catalyst and said gas in said pipe is not substantially greater than the time required for burning-off said carbon deposits and recycling treated catalyst to the reaction vessel.

13. A continuous process for the production of combustible gases which comprises passing a hydrocarbon together with an oxidising gas selected from the class consisting of steam and carbon dioxide over an oxidisable catalyst in a reaction vessel, continuously withdrawing used catalyst bearing deposited carbon from said reaction vessel, feeding withdrawn catalyst to a catalyst regenerating vessel together with a gas containing molecular oxygen to flow in the same direction through said regenerating vessel, controlling the amount of molecular oxygen fed to the regenerating vessel and the rate of flow of used catalyst and gas containing molecular oxygen through the regenerating vessel to ensure that the amount of molecular oxygen and the contact time of said molecular oxygen with used catalyst in said regenerating vessel do not substantially exceed that necessary to burn-off substantially all the deposited carbon, recycling regenerated catalyst to the reaction vessel and recovering sensible heat from the gases issuing from said regenerating vessel.

14. A continuous process according to claim 13 wherein the recovered sensible heat is employed for preheating said oxidising gas.

15. A continuous process according to claim 13 wherein the recovered sensible heat is employed for preheating said gas containing molecular oxygen.

16. A continuous process according to claim 13 wherein the recovered sensible heat is employed for raising steam in a waste-heat boiler.

17. A continuous process according to claim 13 wherein the gas containing molecular oxygen is air.

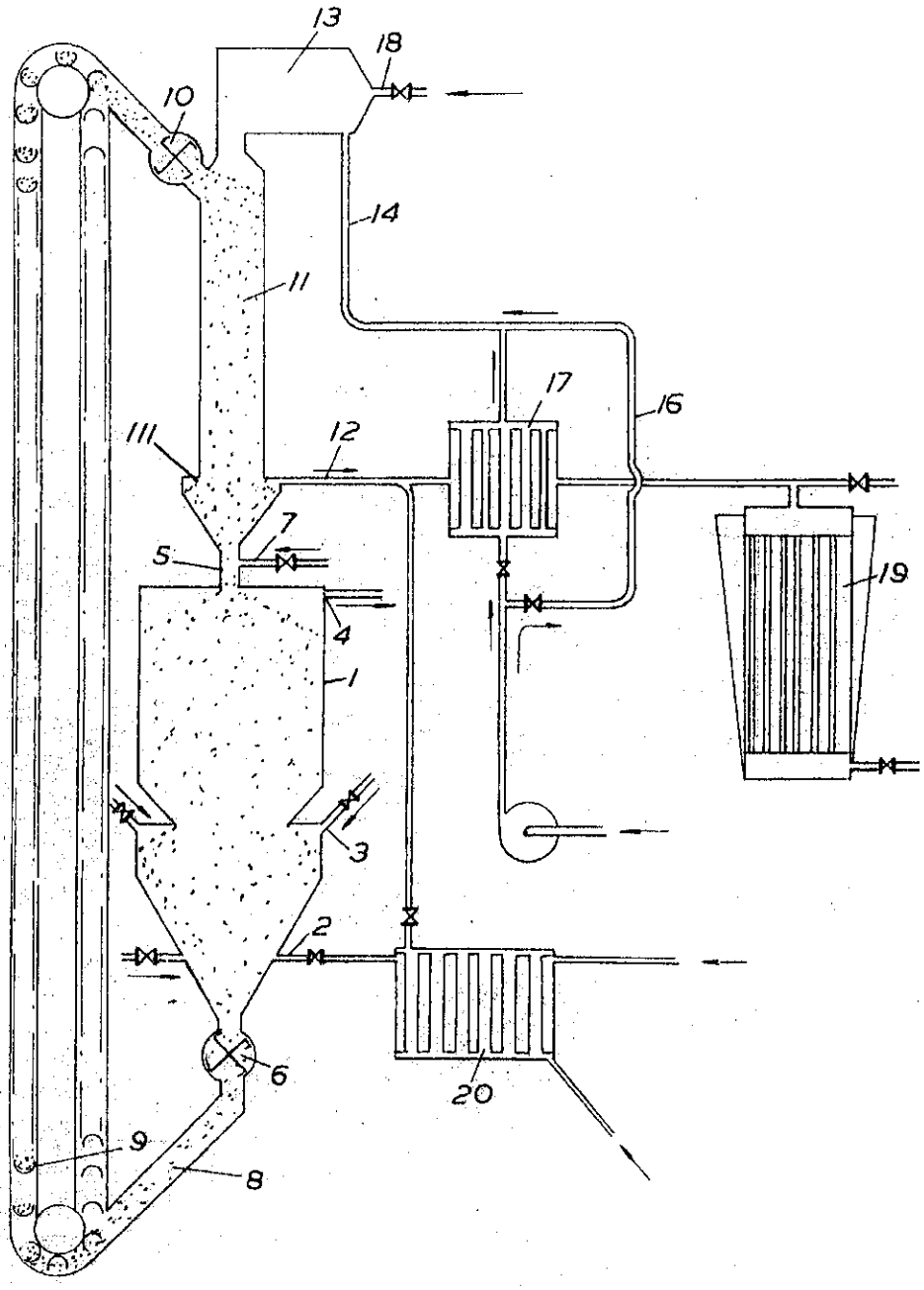
18. A method of removing deposited carbon from a readily oxidisable used catalyst which comprises flowing used catalyst

together with a controlled amount of gas containing molecular oxygen into and through a catalyst regenerating zone, the amount of molecular oxygen and the rate of flow of used catalyst and said gas being so adjusted that burning of carbon from said catalyst is not more than substantially complete at the outlet from said catalyst regenerating zone.

19. A method according to claim 18 wherein a fuel is burnt in said gas containing molecular oxygen before contact with the catalyst in the catalyst regenerating zone.

MI

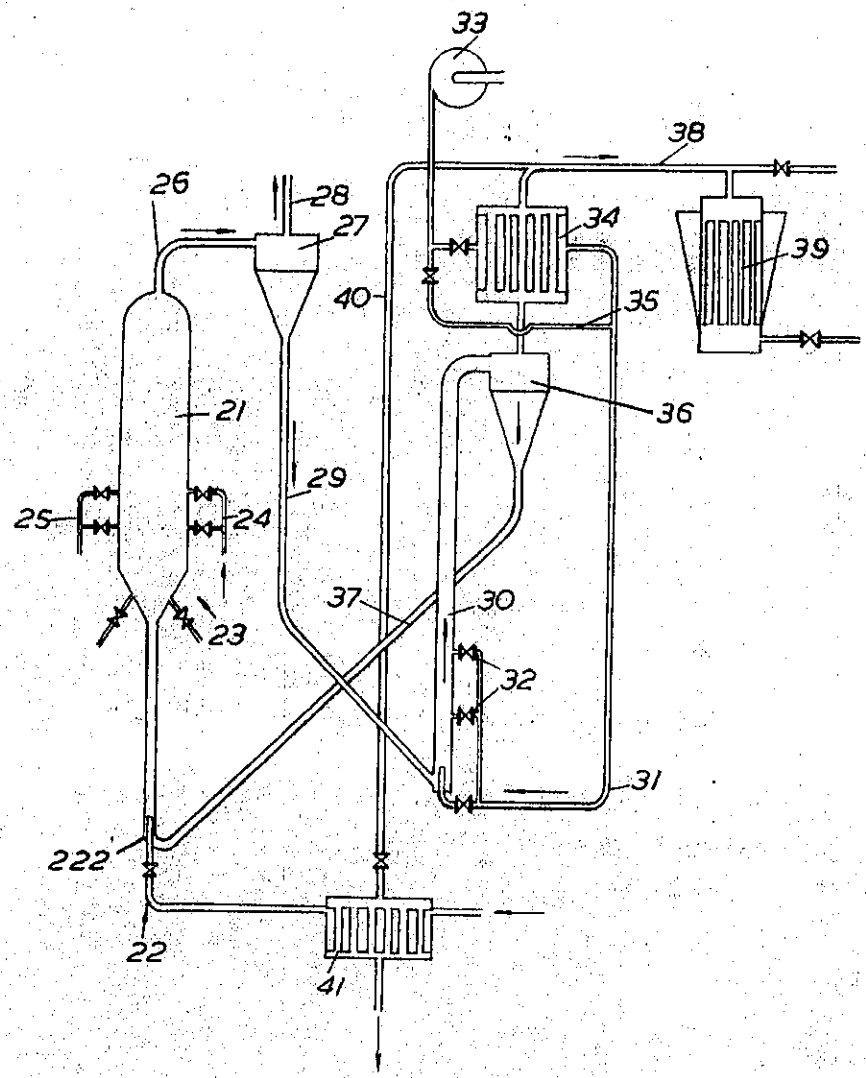
FIG. 1.



INVENTOR
NORMAN HENRY WILLIAMS
PATENT AGENTS

Fetherstonhaugh & Co.

FIG. 2.



INVENTOR
NORMAN HENRY WILLIAMS.
PATENT AGENTS

Fetherstonhaugh & Co