

# PATENT SPECIFICATION

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#### COMPLETE SPECIFICATION

#### Improvements in or relating to Reactors

We, THE BRITISH PETROLEUM COMPANY LIMITED, (previously known as Anglo-Iranian Oil Company Limited), of Britannie House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation and CHANDLER, of the aforesaid Company's address, and of British nationality, do hereby declare the invention for which we pray that a patent may be granted to us, and the 10 method by which it is to be performed to be particularly described in and by the following statement: -

This invention relates to an improved reactor suitable for effecting reaction between 15 one or more reactants in the gaseous phase and one or more reactants in the liquid phase.

It is an object of the present invention to provide an improved reactor for effecting exothermic or endothermic reactions between 20 one or more reactants in the gaseous phase and one or more reactants in the liquid phase. It is a further object to provide a reactor in which the gas flow rate/gas residence time relationship may be subjected to controlled varia-25 tion, thereby imparting improved flexibility to the reaction control.

According to the invention, there is provided a multi-tubular reactor comprising a plutality of reaction tubes which, in the operation posi-30 tion of the reactor, are substantially vertical, the upper ends of said tubes passing through an upper tube plate and the lower ends of said tubes passing through and extending beyoud a lower tube plate, the portion of the 35 tubes between the lower and upper tube plates being enclosed in a shell, whereby the external surfaces of said tubes within said shell may be contacted with a heat exchange medium circulated within said shell, the reactor being 40 bounded below the lower tube plate and above the upper tube plate by enclosed chambers provided with means for the introduction of reactants and means for the withdrawal of products, respectively, the lower ends of at 45 least some of the reaction tube, being pro-

vided with gas distributing means, whereby, in operation, a stream of small bubbles of the gaseous phase reactant is caused to ascend through the liquid phase reactant within each tube, provided with said means.

Usually the reactor will contain between 20 and 500 reaction tubes. The invention is however in no way limited in this respect and a larger or smaller number of reaction tubes may be employed if desired.

The gas distributing means may take the form of cut away sections at or near the lower ends of a reaction tube. Alternatively the lower ends of the tube may be fitted with porous rings or plugs, for example, of sintered metal, ceramic material, wire gauze or of fibrous material.

In operation, the gaseous feed passes into the bottom chamber of the reactor, collecting to form a gaseous phase zone in the space around the extensions of the reaction tubes below the tube plate, and thence bubbles up each tube through the distributing device. A gas/liquid interface is formed at the lower end of the reaction tubes. An advantage of this 70 method lies in the fact that the distributing device is unlikely to become choked as it is subject to the washing action of the liquid reaction mixture. A further advantage lies in the simplicity of the fed connections to the base of the reactor. Yet another advantage lies in the fact that when tubes of small diameter are employed the bubbles of gas pass up in proximity to the walls of the rubes and the reaction can take place adjacent to the surface through which heat is being re-moved or supplied by means of the heat exchange medium. Yer another advantage lies in the fact that the gas flow rate may be varied over a wide range without altering 85 appreciably the pressure of the gas.

When employing a continuous liquid feed, the liquid may be introduced into the bottom chamber and removed from the top chamber.

In a modification of this type of reactor 90

[Price 3s, Od.]

there is also provided at least one down flow tube, substantially parallel to the reaction tubes, said down flow tube passing through the upper and lower tube plate and terminating at its lower end below the ends of the reaction tubes. The liquid in a reactor of this type will circulate up the tubes through which gas is passing and down the tubes extending into the liquid in the borrom chamber of the reactor, and is especially suitable for use in cases wherein the gas dissolves with relative ease in the reaction mixture but wherein the reaction in the liquid phase is relatively slow.

In a further modification of the reactor, at 15 least one vertical baffle is provided within the lower chamber, being attached to the lower tube plate, whereby the upper portion of the lower chamber is divided into at least two compartments, means being provided for the separate introduction of gaseous reactant to each of said compartments. The compartments can be interconnected below the level of the

liquid.

By adjusting the amount of gas fed to each 25 compartment, the gas residence time in the reactor can be varied. With the gaseous feed passing to both or all of the compartments in the bottom chamber of the reactor, bubbles of gas of a relatively small size will pass up 30 the tubes provided for gas flow and, because they are small, these bubbles will travel relatively slowly through the liquid in the tubes. Thus the residence tune of the gas in the reactor will be relatively long. If now the gaseous feed is passed to one or a smaller number than before, of the compartments in the bottom chamber of the reactor, but at the same total rate as before, the bubbles of gas being larger will travel faster and the residence time of the gas will be shorter and, under conditions of continuous liquid feed, that of the liquid correspondingly longer.

Alternatively, it may be desirable to alter the gas flow, for example by recycling more or less gas, while maintaining the residence time constant. This may be done by aftering the number of compartments to which gas is fed in the borrow chamber of the reactor.

The reactors according to the present invention are particularly suitable for carrying out either exothermic reactions or endothermic reactions. In the former case, a coolant is circulated in the reactor shell, while in the latter case, a hearing medium is circulated. 55 In either case, an improvement may be effected in the control of reactions by the use of the present reactor in consequence of its characteristic features whereby the initial stage of the reaction takes place in the sections of the fe-60 actor tubes which are not in contact with the hear exchange medium. Thus in an endothermic reaction the temperature of the reaction mixture in the bottom few inches of the tubes will be high, thereafter falling 65 rapidly to a minimum and thereafter gradually

rising. In an exothermic reaction the temperature of the reaction mixture will be initially low, thereafter rising rapidly to a maximum before falling gradually along the length of the tubes. It is believed that these temperature characteristics are, in fact, a result of the time lag caused by the gas having to dissolve in the reaction mixture, followed by a rapid initial rate of reaction which falls away as the concentrations of reactants and products approach equilibrium values. The length of the extension of the reactor tubes below the bottom tube plate can be made so that the nainimum temperature (for endothermic reactions) or maximum temperature (for exothermic reactions) is reached just above the bottom tube plate where the heating or cooling medium is introduced into the shell. The velocity of the medium may be made greater where the greatest transfer of heat is required, 85 by mcans of baffles.

The reactor according to the present invention may be used for effecting any of a wide variety of chemical reactions for example halogenation, hydrogenation, oxidation, hydroformylation, alkylation and polymerization, of which the following are specific examples: ---

1. The OXO reaction between propylene, carbon monoxide and hydrogen with cobalt carbonyl catalyst to make butyraldehydes.

2. Oxidation with air or oxygen of light. hydro-carbon mixtures to make fatty acids.

Air blowing of vegetable oils,

The invention is illustrated but in no way limited with reference to Figures I-9 accom- 100 panying the Provisional specification.

Figures 1-3 illustrate three types of reactor according to the present invention.

Figures 4-9 illustrate different gas distributing devices which may be employed at the 105 lower ends of the reactor types.

With reference to Figure 1:-

The reactor comprises a plurality of parallel vertical rubes 1, (five shown) attached at their upper ends to a tube plate 2 and, near their lower ends, passing through tube plate 3. Tube plates 2 and 3 constitute end sections to a reactor shell, bounded by outer wall 4 having attached thereto input and offtake pipes 5 and 6 respectively for a heat exchange medium. To tube plate 2 is bolted domed casing 7 having a product offrake pipe 8 attached thereto. To tube plate 3 is bolted domed vessel 9 having, attached thereto, reactable input pipe

Tubes 1 are provided, at their lower extremities, with gas distribution means as hereinbefore described, and more particularly described hereinafter with reference to Figures 4-9. Baffles 11 and 12 are provided within 125 the reactor shell 4.

With reference to Figure 2:-

The reactor comprises a plurality of parallel vertical tubes 21, (three shown) attached near their upper ends to tube plate 22 and, ex- 130

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tending a short distance above said plate 22 and, near their lower ends, passing through tube plate 23. The reactor also comprises a plurality of parallel vertical tubes 24 (two shown) attached near their upper ends to said tube plate 22 and terminating below the level of the upper ends of tubes 21, said rubes 24 also passing through tube plates 23. Tubes 21 extend below tube plate 23 and are provided, at their lower extremities, with gas distributing means, as hereinbefore described. Tubes 24 extend below said tube plate 23 and terminate at a level below the lower extremities of tubes 21. Tube plates 22 and 23 constitute end sections to a reactor shell, bounded by outer wall 25 having attached thereto input and offtake pipes 26 and 27 respectively for a heat exchange medium. To tube plate 22 is bolted domed casing 28 having a product offtake pipe 29 attached thereto. To tube plate 23 is bolted domed vessel 30 having attached thereto, reactant input pipes 31. Baffles 32 as provided within the reactor shell. With reference to Figure 3:-The reactor comprises a plurality of parallel

tubes 41 (four shown) attached near their upper ends to tube plate 42, extending a short distance above said plate 42, and near their lower ends, passing through tube plate 43. 30 The reactor also comprises a plurality of parallel vertical tubes 44 (two shown) attached near their upper ends to said tube plate 42 and rerminating below the level of the upper ends of tubes 41, said tubes 44 also passing through plate 43. Tubes 41 extend below tube plate 43 and are provided, at their lower extremities with gas distributing means, as hereinbefore described. Tubes 44 extend below said tube plate 43 and tenminate at a level below the lower extremities of tubes 41 .Tube plates 42 and 43 constitute end sections to a reactor shell bounded by outer wall 45 having attached thereto input and offtake pipes 46 and 47 respectively for a heat exchange medium. To tube plate 42 is bolted domed casing 48 having a product offtake pipe 49 attached thereto. To tube plate 43 is bolted domed vessel 50 having attached thereto re-actor input pipes 51. Tube plate 43 has 50 attached thereto and downwardly depending therefrom a vertical baffle 52 terminating below the level of tubes 44 and effectively dividing the chamber within casing 50, into two compartments. Horizontal baffles 53 are provided within the reactor shell Figures 4

to 9 illustrate different gas distributing means which may be employed at the lower extremities of tubes 1, 21 and 41 described

In Figures 4 and 5 distribution is controlled by serrations as shown. Figure 6 illustrates a system of inlet ports. Figure 7 depicts a porous ring, attached to the lower edge of the urbe wall, through which ring reactant 65 gas permeates. Figure 8 depicts a rapered, serrated tube end. Figure 9 illustrates a tapered porous plug.

What we claim is:-

1. A multi-tubular reactor for effecting reactions, between at least one reactant in the 70 gaseous phase and at least one reactant in the liquid phase, which necessitate, for their control, the transference of heat between the reactants and a head exchange medium, said reactor comprising a plurality of reaction tubes which, in the operating position of the reactor, are substantially vertical, the upper colds of said tubes passing through an upper tube plate and the lower ends of said tubes passing through and extending beyond a lower tube plate, the portion of the tubes between the lower and upper tube plates being enclosed in a shell, whereby the external surfaces of said tubes may be contacted with a heat exchange medium circulated within said shell, the reactor being bounded below the lower tube plate and above the upper tube plate by enclosed chambers provided with means for the introduction of reactants and means for the withdrawal of products, respectively, the lower ends of at least some of the reaction tubes being provided with gas distributing means, whereby, in operation, a stream of small bubbles of the gaseous phase reactant is caused to ascend through the liquid phase reactant within each tube provided with said means.

2. A reactor to claim 1 in which there is provided at least one down flow tube, substantially parallel to the reaction tubes, said down flow tube passing through the upper and 100 lower tube plate and terminating at its lower. end below the ends of the reaction tubes.

3. A reactor according to claim 1 or 2 in which at least one vertical baffle is provided within the lower chamber, artached to the 105 lower tube plate, whereby the upper portion of said lower chamber is divided into at least two compartments, means being provided for the separate introduction of gaseous reactant to each of said compartments.

4. A reactor according to any of the preceding claims in which the shell is provided with horizontal baffles to control the path of the heat exchange medium through the shell.

5. A reactor according to any of the pre- 115 ceding claims in which the gas distributing means consist of a porous ring attached to the lower edge of the wall of a reaction rube.

6. A reactor according to any of claims 1-4 in which the reaction tubes have the 120 periphery of their lower ends serrated.

7. A multi-tubular reactor, for effecting reactions between at least one reactant in the gaseous phase and at least one reactant in the liquid phase, substantially as hereinbefore 125 described with reference to any of Figures 1-3 accompanying the Provisional Specification.

8. A multi-tubular reactor, as claimed in any of claims 1-4 or 7 having gas distri- 130

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buting means substantially as hereinbefore desóribed with reference to any of Figures 4—9 accompanying the Provisional Specification.

T. MIACDONALD, For the Applicants.

### PROVISIONAL SPECIFICATION

## Improvements in or relating to Reactors

We, Anglo-Iranian Oil Company
Limited, of Britannic House, Finsbury
Circus, London, E.C.2, a British jointstock Corporation and Richard Chandler
of the aforesaid Company's address and of
British nationality do hereby declare this into vention to be described in the following
statement:—

This invention relates to an improved reactor suitable for effecting reaction between
one or more reactants in the gaseous phase
and one or more reactants in the liquid phase.
More particularly it relates to a reactor suitble for effecting reactions of the above type,
which are appreciably exothermic or endothermic.

According to the invention, there is provided a multi-tubular reactor comprising a plurality of tubes, which, in the operating position of the reactor, are substantially vertical, said tubes terminating at their upper ends in an upper tube plate and having their lower ends extending through a lower tube plate, the portion of the tubes between the lower and upper tube plates being enclosed in a shell, whereby their external surfaces may be contacted with a heat exchange medium.

The reactor is bounded bellow the lowest tube plate and above the upper tube plate by enclosed chambers provided with means for the introduction of reactants and withdrawal of products, respectively.

Preferably the lower ends of the tubes are each provided with gas distributing means, whereby, in operation, a stream of small bubbles of the gaseous phase reactant is caused to ascend through the liquid phase reactant, within each tube, in proximity to the wall of said tube.

The gas distributing means may take the form of cut away sections at or near the lower ends of the tube. Alternatively the lower ends of the tube may be littled with perous rings or plugs, for example, of sintered metal, ceramic material, wire gauze or of fibrous 50 material.

The gaseous feed passes into the bottom chamber of the reactor, collecting in the space around the extensions of the tubes below the tube plate, and thence bubbles up each tube through the distributing device. An advantage of this method lies in the fact that the distributing device is unlikely to become choked as

it is subject to the washing action of the liquid reaction mixture. A further advantage lies in the simplicity of the feed connections to the base of the reactor. Yet another advantage lies in the fact that the bubbles of gas pass up near the walls of the tubes and the reaction can take place adjacent to the surface through which heat is being removed or supplied by means of the heat exchange medium.

In a modification of this type of reactor some tubes are constructed as described and other tubes extend downwards from the bottom tube plate to have their lower ends at a level below that of the tubes which are equipped with distributing means. The liquid in such a reactor will circulate up the tubes through which gas is passing and down the tubes extending into the liquid in the bottom chamber of the reactor, and is especially suitable for use in cases wherein the gas dissolves with relative case in the reaction suitature but wherein the reaction in the liquid phase is relatively slow.

In a further modification of this type of reactor the bottom chamber is divided into two or more compartments with separate gas feed to each compartment. The compartments can be interconnected below the level of the liquid. By adjusting the amount of gas fed to each compartment, the liquid and gas residence times in the reactor can be varied.

The reactors according to the present invention are particularly suitable for carrying out either exothermic reactions or endothermic reactions. In the former case, a coolant is circulated in the reactor shell, while in the latter case, a heating medium is circulated. In either case, an improvement may be effected in the control of reactions by the use of the present reactor in consequence of its characteristic features whereby the initial stage of the reaction takes place in the sections of the reactor tubes which are not in contact with the heat exchange medium. Thus in an endothermic reaction the temperature of the reaction mixture in the bottom few inches of the tubes will be high, thereafter falling 105 rapidly to a minimum before rising gradually. In an exothermic reaction the temperature of the reaction mixture will be initially low, thereafter rising rapidly to a maximum before falling gradually along the length of the tubes. 110 It is believed that these temperature charac-

teristics are, in fact, a result of the time lag caused by the gas having to dissolve in the reaction mixture followed by a rapid initial rate of reaction which falls away as the concentrations of reactants and products approach equilibrium values. The length of the extension of the reactor tubes below the bottom tube plate can be made so that the minimum temperature (for endothermic re-10 actions) or maximum temperature (for exothermic reactions) is reached just above the bottom tribe pizte where the heating or cooling medium is introduced into the shell. The velocity of the medium may be made greater 15 where the greatest transfer of heat is required, by means of baffles.

The reactor according to the present invention may be used for effecting any of a wide variety of chemical reactions of which

20 the following are illustrated: -

 The OXO reaction between propylene, carbon monoxide and hydrogen with cobalt carbonyl catalyst to make butyraldehydes.

 Oxidation with air or oxygen of light hydro-carbon mixtures to make fatty acids.

3. Air blowing of vegetable oils.

The invention is illustrated but in no way limited by the accompanying Figures 1—9. Figures 1—3 illustrate three types of reactor according to the present invention.

30 actor according to the present invention.

Figures 4—9 illustrate different gas distributing devices which may be employed at the lower ends of the reactor types.

With reference to Fig. 1:--

The reactor comprises a plurality of parallel vertical tubes 1, (five shown) attached at their upper ends to a tube plate 2 and, near their lower ends, passing through tube plate 3. Tube plates 2 and 3 constitute end sections to a reactor shell, bounded by outer wall 4 having attached thereto input and off-take pipes 5 and 6 respectively. To tube plate 2 is belted domed casing 7 having a product offtake pipe 8 attached thereto. To tube plate 3 is belted domed vessel 9 having, attached thereto, reactant input pipe 10.

Tubes 1 are provided, at their lower extremities, with gas distributing means as hereinbefore described, and more particularly described hereinafter with reference to Figures 4—9. Baffles 11 and 12 are provided within the reactor shell 4.

With reference to Fig. 2:-

The reactor comprises a plurality of parallel vertical tubes 21, (three shown) attached near their upper ends to tube plate 22 and, extending a short distance above said plate 22 and, near their lower ends, passing through tube plate 23. The reactor also comprises a foundative of parallel vertical tubes 24 (two

shown) attached near their upper ends to said tube plate 22 and terminating below the level of the upper ends of tubes 21, said tubes 24 also passing through tube plates 23. Tubes 21 extend below tube plate 25 and are provided, at their lower extremities, with gas distributing means, as hereinbefore described. Tubes 24 extend below said tube plate 23 and terminate at a level below the lower extremities of tubes 21. Tube plates 22 and 23 constitute end sections to a reactor shell, bounded by outer wall 25 having attached thereto input and offtake pipes 26 and 27 respectively. To tube plate 22 is belted domed casing 28 having a product offtake pipe 29 attached thereto. To tube plate 23 is belted domed domed vessel 30 having attached thereto, reactant input pipe 31.

With reference to Fig. 3:—

The reactor comprises a plurality of parallel vertical tubes 41 (four shown) attached near their upper ends to tube plate 42, extending a short distance above said plate 42 and, near their lower ends, passing through tube plate 43. The reactor also comprises a plurality of parallel vertical tubes 44 (two shown) attached near their upper ends to said tube plate 42 and terminating below the level of the upper ends of tabes 41, said rubes 44 also passing through plate 4B. Tubes 41 extend below tube plate 43 and are provided, at their lower extremities with gas distributing means, as hereinbefore described. Tubes 44 extend below said tube plate 43 and terminate at a level below the lower extremities of tubes 41. Tube plates 42 and 43 constitute end sections to a reactor shell bounded by outer wall 45 having artached thereto input and offtake pipes 46 and 37 respectively. To tube plate 42 is bulted domed casing 48 having a product offtake pipe 49 attached thereto. To tube plate 43 is bolted domed vessel 50 having attached thereto reactor input pipe 51. Tube plate 43 has attached thereto and downwardly depending therefrom a vertical baffle 52 terminating below the level of tubes 44 and effectively dividing the chamber within casing 50, into two compartments. Figs. 4 to 9 Hustrate different gas distributing means which may be employed at the lower extremities of tubes 1, 21 and 41 described above.

In Figs. 4 and 5 distribution is controlled by serrations as shown. Fig. 6 illustrates a system of inlet ports. Fig. 7 depicts a porous ring, attached to the tube wall and through which reactant gas permeates. Fig. 8 depicts a tapered, serrated tube end. Fig. 9 illustrates a tapered porous plug.

T. MACDONALD For the Applicants.

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742,931 PROVISIONAL SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale.



