(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 447 092 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification : **27.07.94 Bulletin 94/30**

(51) Int. Cl.^{5} : **C10G 65/08**

(21) Application number : **91301780.2**

(22) Date of filing : **04.03.91**

(54) **Method of producing food grade quality white mineral oil.**

(30) Priority : **12.03.90 US 491511**

(43) Date of publication of application : **18.09.91 Bulletin 91/38**

(45) Publication of the grant of the patent : **27.07.94 Bulletin 94/30**

(84) Designated Contracting States : **AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

(56) References cited :
GB-A- 2 001 339
US-A- 4 325 804
Hawley's Chemical Dictionary, 11th Edition, Van Nostrand Reinhold Company, (1987), page 616

(73) Proprietor : **ATLANTIC RICHFIELD COMPANY**
515 South Flower Street
Los Angeles California 90071 (US)

(72) Inventor : **Everett, Gary L.**
2640 Silver Falls Drive
Kingwood, Texas 77339 (US)

(74) Representative : **Cropp, John Anthony David et al**
MATHYS & SQUIRE
10 Fleet Street
London, EC4Y 1AY (GB)

Jouve, 18, rue Saint-Denis, 75001 PARIS

Description

SPECIFICATION

Field of the Invention

This invention relates to the method of producing food grade quality white mineral oil. More particularly, this invention relates to a method of producing from a naphthenic distillate as a feedstock, a food grade white mineral oil with only a trace of aromatics therewithin.

Background of the Invention

The prior art is replete with various referrals to methods of treating hydrocarbons. These range from the technology during the depression to modern methods of treating hydrocarbons.

There are almost as many references to employing hydrogen in hydrogenation and hydrotreating aspects. Included are a couple of textbooks published right after World War II including "The Textbook of Organic Chemistry" by E. Wertheim, Second Edition, Blakiston Company, Philadelphia, Pennsylvania, 1947, and "Unit Processes in Organic Synthesis", Groggins, Editor, a3rd Edition, McGraw Hill, New York, New York, 1947. As pointed out in these texts, careful control of hydrogenation can give careful results. This application envisions employing such careful control.

The prior art has seen many ways of trying to achieve a food grade quality of white mineral oil but they have always been expensive and employed acid treatment, neutralization and an adsorption tower or the like for removing of undesired constituents to give the final product.

Specifically, the prior art has failed to provide an economical method of achieving a food grade quality white mineral oil without expensive and labor intensive steps such as acid treating, neutralization and adsorbing of undesired constituents from the product.

US-A-4325804 describes a process for the production of a food grade quality white mineral oil from a hydrocarbon feedstock by means of a series of hydroprocessing steps. However, the process requires a hydrocracking step which has the disadvantage that it requires high energy consumption levels and converts much of the aromatic content of the feedstock into a product having a non-white oil boiling range.

It is a specific object of this invention to provide an economical continuous flow process of providing a food grade white mineral oil which overcomes the aforementioned disadvantages.

According to the present invention, therein provided a method for the production of food grade quality white mineral oil from a naphthenic feedstock without solvent extraction or acid treatment in a continuous process wherein the feedstock is subjected to a plurality of hydroprocessing steps in series characterised in that

(i) said feedstock is subjected to three stages of hydrogenation;

(ii) the first stage hydrogenation is conducted at a temperature in the range of 288°C to 399°C (550°F to 750°F) and with a hydrogen partial pressure of at least 8.2 MPa gauge (1200 psig) but less than 13.7 MPa gauge (2000 psig).

(iii) the feed to the second step comprises liquid product from the first step, and

(iv) the feed to the third step comprises liquid product from the second step.

By means of the invention it is possible to obtain a mineral oil of the final desired quality with only a trace of the aromatic hydrocarbons, or aromatic carbons, therewithin.

In one preferred embodiment, the feedstock is first hydrogenated followed by a step of separating gaseous constituents produced during the hydrogenation reaction, followed by a second stage of hydrogenation, followed by separation of the gaseous constituents produced by this second stage of hydrogenation, followed by a third and less severe hydrogenation step to produce the desired food grade white mineral oil.

Specific reaction conditions for the respective steps are discussed hereinafter.

The invention will now be described in greater detail with reference to preferred embodiments and with the aid of the accompanying drawings in which

Fig. 1 is a schematic flow diagram of a prior art process for producing food grade white mineral oil; and

Fig. 2 is a schematic flow diagram of the process of this invention for producing food grade white mineral oil.

Description of Preferred Embodiments

Fig. 1 illustrates a prior art method of preparing a food grade white mineral oil. Therein a napthenic distillate is extracted with a solvent such as a phenol or N-methyl pyrrolidine to produce a hydrocarbon oil containing only 4 to 7 percent aromatic carbons which is subjected to an acid treatment. The bottoms fraction recovered from the acid treatment then emerges as acid sludge whereas from the first step of solvent extraction, a solvent extract containing a high level of aromatic compounds is recovered as a bottom product. After the acid treatment, only a trace of aromatic carbons, or aromatic hydrocarbons, is in line 15 leading from the acid treater. A finishing step consisting of an adsorption tower 17 employing clay or a hydrotreater tower 17 using hydrogen is employed to lower the remaining trace quantity of aromatics and product

a satisfactory food grade white mineral oil in the effluent line 19.

In contrast, the approach of this invention involves subjecting a naphthenic distillate illustratively containing a concentration of aromatic carbons in the range of 15 - 25 percent by weight, to hydrogenation to produce a hydrogenated product in which there is a reduction of 50 to 70 percent of the aromatic hydrocarbons to yield an aromatic carbon content of 7 - 10 percent by weight. This is shown in Fig. 2, at stage 1, also labeled tower 21. The term "naphthenic distillates" is synonymous with cycloparaffinic distillates. Normally these distillates contain about 15 - 25 percent by weight of aromatic carbons. These naphthenic distillates come in via line 23, Fig. 2. Hydrogen is fed through line 25 in Fig. 2. Both feed constituents are admixed prior to entering stage 1 where hydrogenation is carried out in the presence of a hydrogenation catalyst containing metal components from the Group VIIIA class, preferably Nickel and from the Group VIA class, preferably Molybdenum at a temperature of 288°C to 399°C (550 degrees Fahrenheit to 750 degrees Fahrenheit), preferably 343°C to 371°C (650 degrees Fahrenheit - 700 degrees Fahrenheit) with a partial pressure of hydrogen in the range of 8.2 - 13.7 MPa gauge (1200 - 2000 pounds per square inch gauge (PSIG)), preferably 10.3 - 12.4 MPa (1500 - 1800 pounds per square inch) gauge. The hydrogenated product then exits the tower 21 through the line 27.

As the next step, the gaseous constituents of the hydrogenated product in line 27 are separated from liquid constituents and flow out through the overhead line 29. The overhead line 29 carries from the stripper 31 hydrogen sulfide and ammonia, inter alia, as the gaseous products of the hydrogenation reactions carried out in the hydrogenation tower of stage 1, labelled 21. After this process, the aromatic carbon content of the liquid constituents will have been reduced to about 7 - 10 percent aromatic carbons as in the liquid bottom draw from the stripper, line 33. These liquid bottoms containing only about half as much aromatic carbons as the initial feedstock in line 23, or less, are then sent through line 35 to a second hydrogenation tower 37. The liquid bottoms, or hydrogenated product from the first stage, in line 35 is admixed with hydrogen by way of line 39. A second hydrogenation is carried out at rather severe conditions in the presence of a hydrogenation catalyst containing metal components from the Group VIIIA class, preferably Nickel and from the Group VIA class, preferably Molybdenum, with the hydrogen partial pressure in the range of 17.3 - 20.7 MPa gauge (2500 - 3000 PSIG), preferably 19.0 - 20.7 MPa gauge (2750 - 3000 PSIG) and a temperature in the range of 302°C - 399°C (575 - 750 degrees Fahrenheit), preferably 329°C - 371°C (625 - 700 degrees Fahrenheit). The entire reactor effluent then exits by a line 41 to stripper 43 and again the gaseous constituents of the second hydrogenation stage reaction product are separated from liquid constituents and exit line 45 from the second stripper 47. These gaseous constituents include hydrogen sulfide and ammonia, inter alia. The resulting liquid bottoms from the stripper 43, in line 49, contain only about 1 percent of aromatic carbons and they are sent, as by line 51 to be admixed with hydrogen in line 53 and the hydrogenation as a final step is carried out in stage 3, or the final, less severe hydrogenation of stage 3 in the hydrogenation tower 55.

In the final step, less severe hydrogenation of stage three in the third hydrogenation tower, or hydrotreating tower 55, is carried out in the presence of a hydrogenation catalyst containing a metal component of Group VIIIA class such as platinum, palladium or Nickel, preferably platinum in the form usually utilized in reforming reactions with hydrogen partial pressure in the range of 13.7 - 20.7 MPa gauge (2000 - 3000 PSIG), preferably 17.2 MPa - 20.7 MPa gauge (2500 - 3000 PSIG) and temperature of only 191°C to 316°C (375 degrees Fahrenheit to 600 degrees Fahrenheit), preferably 232°C - 288°C (450 degrees Fahrenheit - 550 degrees Fahrenheit).

It is noteworthy that in all these reactions, the use of a relatively high partial pressure of hydrogen and relatively lower temperature facilitates carrying out the hydrogenation to give the desired reaction product in reducing the aromatic constituents of the liquid stream without excessive cracking of the stream to undesired lower boiling range material.

In the illustrated embodiment, the liquid bottoms draw in the line 57 will have only about 0.3 percent or less by weight of aromatic constituents and this trace of aromatics is satisfactory as a food grade white mineral oil. Specifically, the polynucular aromatics will comprise less than 30 parts per million (PPM) of the final food grade white mineral oil.

In operation, the naphthenic distillate comprising the initial feedstock is fed into and admixed with the hydrogen at the desired partial pressure in the incoming stream and hydrogenation is carried out in stage 1. Similarly, in a stripper, the gaseous constituents are allowed to separate from the liquid constituents such that the gases pass out the overhead stream in line 29 and the bottoms pass out the liquid stream 33 and are then fed through the line 35, Fig. 2, to the second stage, or hydrogenation tower, 37. Again, the admixture of hydrogen at its high partial pressure with the liquid constituents effects a direct reaction at elevated temperatures over suitable catalyst to produce the reduction in the aromatic carbons in line 41 such that after the gaseous constituents are separated and go to the overhead line 45, the liquid bottom draw 49 can be fed, low as it is in aromatic carbons, to the third hydrogenation stage 55. At the entrance to the third stage, it is admixed with high pressure hydrogen at the desired high partial pressure and the hydrogen-

ation reactions carried out in the third hydrogenation tower 55. The result is that the final product comes out the bottom effluent line 57.

From the foregoing it can be seen that the desired food grade quality white mineral oil is produced in the line 57 by a process that differs substantially from the prior art technology for preparing food grade white mineral oil.

Claims

1. A method for the production of food grade quality white mineral oil from a naphthenic feedstock without solvent extraction or acid treatment in a continuous process wherein the feedstock is subjected to a plurality of hydroprocessing steps in series characterised in that
   (i) said feedstock is subjected to three stages of hydrogenation;
   (ii) the first stage hydrogenation is conducted at a temperature in the range of 288°C to 399°C (550°F to 750°F) and with a hydrogen partial pressure of at least 8.2 MPa gauge (1200 psig) but less than 13.7 MPa gauge (2000 psig);
   (iii) the feed to the second step comprises liquid product from the first step; and
   (iv) the feed to the third step comprises liquid product from the second step.

2. A method as claimed in claim 1 comprising the steps of:
   a. reducing the aromatic content of the feed by about 50% in a first hydrogenation step;
   b. separating the gaseous constituents from the hydrogenated liquid product from step (a);
   c. reducing the aromatic carbon content of the liquid product from step (a), after the gaseous constituents have been separated therefrom, to about one percent by submitting said product to a second hydrogenation step;
   d. separating the gaseous product constituents of the hydrogenation product of step (c); and
   e. producing the food grade quality white mineral oil with only a trace of aromatics therewithin by subjecting the liquid product from step (c), after the gaseous constituents have been separated therefrom, to a final hydrogenation step under conditions which are less severe than those of step (a) and step (b)

3. A method as claimed in claim 1 or claim 2 wherein the feed is a naphthenic or cycloparaffinic distillate containing a concentration of aromatic carbons in the range of 15 - 25 percent by weight.

4. The method of claim 3 wherein said first hydrogenation is carried out with a nickel molybdenum catalyst and said gaseous constituents of said hydrogenated product comprise hydrogen sulfide and ammonia which are separated by stripping.

5. The method of claim 3 or claim 4 wherein said first hydrogenation is carried out with a partial pressure of hydrogen in the range of 10.3 - 12.4 MPa (1500 - 1800 PSIG); and a temperature in the range of a 343 - 371°C (650 - 700 degrees Fahrenheit).

6. The method of any one of claims 2 to 5 wherein said second hydrogenation is carried out with a nickel molybdenum catalyst and said gaseous constituents of said second hydrogenated product comprise hydrogen sulfide and ammonia which are separated by stripping.

7. The method of claim 6 wherein said partial pressure of said hydrogen is in the range of 19.0 - 20.7 MPa (2750 - 3000 PSIG) and wherein said temperature is in the range of 329 - 371°C (625 degrees Fahrenheit - 700 degrees Fahrenheit).

8. The method of any one of claims 2 to 7 wherein said final, less severe hydrogenation is carried out in the presence of a platinum reforming catalyst.

9. The method of claim 8 wherein said final, less severe, hydrogenation is carried out with a partial pressure of hydrogen being in the range of 17.2 - 20.7MPa (2500 - 3000 PSIG) and said temperature being in the range of 232 - 288°C (450 degrees Fahrenheit - 550 degrees Fahrenheit).

Patentansprüche

1. Verfahren zur Herstellung eines weißen Mineralöls (Weißöls) von Lebensmittelqualität aus einem naphthenischen Ausgangsmaterial ohne Lösungsmittelextraktion oder Säurebehandlung in einem kontinuierlichen Prozeß, bei dem das Ausgangsmaterial einer Vielzahl von aufeinanderfolgenden Hydrierverfahrensschritten unterworfen wird, dadurch gekennzeichnet, daß
   (i) das Ausgangsmaterial drei Hydrierungsstufen unterworfen wird;
   (ii) die erste Hydrierungsstufe bei einer Temperatur im Bereich von 288°C bis 399°C (550°F bis 750°F) und einem Wasserstoffpartialdruck von mindestens 8,2 MPa (1200 psig), aber weniger als 13,7 MPa (2000 psig) durchgeführt wird;
   (iii) die Beschickung zur zweiten Stufe flüssi-

ges Produkt aus der ersten Stufe umfaßt und (iv) die Beschickung zur dritten Stufe flüssiges Produkt aus der zweiten Stufe umfaßt.

2. Verfahren nach Anspruch 1 mit den Schritten
a. Verringerung des Aromatengehalts der Beschickung um etwa 50 % in einer ersten Hydrierungsstufe;
b. Abtrennung der gasförmigen Bestandteile aus dem hydrierten flüssigen Produkt aus Stufe (a);
c. Verringerung des Gehalts an aromatischen Kohlenstoffen im flüssigen Produkt aus Stufe (a) nach Abtrennung der gasförmigen Bestandteile auf etwa ein Prozent, indem das Produkt einer zweiten Hydrierungsstufe unterworfen wird.
d. Abtrennung der gasförmigen Produktbestandteile des Hydrierungsproduktes aus Stufe (c) und
e. Herstellung eines weißen Mineralöls (Weißöls) von Lebensmittelqualität, das nur spurenweise Aromaten enthält, indem das Produkt aus Stufe (c) nach Abtrennung der gasförmigen Bestandteile daraus unter Bedingungen, die weniger streng sind als in Stufe (a) und Stufe (b), einer letzten Hydrierungsstufe unterworfen wird.

3. Verfahren nach Anspruch 1 oder 2, bei dem die Beschickung ein naphthenisches oder cycloparaffinisches Destillat ist, das eine Konzentration von aromatischen Kohlenstoffen im Bereich von 15 - 25 Gew.-% aufweist.

4. Verfahren nach Anspruch 3, bei dem die erste Hydrierung mit einem Nickel-Molybdän-Katalysator durchgeführt wird und die gasförmigen Bestandteile des hydrierten Produkts Schwefelwasserstoff und Ammoniak enthalten, die durch Strippen abgetrennt werden.

5. Verfahren nach Anspruch 3 oder 4, bei dem die erste Hydrierung bei einem Wasserstoffpartialdruck im Bereich von 10,3 - 12,4 MPa (1500 - 1800 psig) und einer Temperatur im Bereich von 343°C - 371°C (650F°- 700°F) durchgeführt wird.

6. Verfahren nach einem der Ansprüche 2 bis 5, bei dem die zweite Hydrierung mit einem Nickel-Molybdän-Katalysator durchgeführt wird und die gasförmigen Bestandteile des zweiten hydrierten Produkts Wasserstoff und Ammoniak umfassen, die durch Strippen abgetrennt werden.

7. Verfahren nach Anspruch 6, bei dem der Wasserstoffpartialdruck im Bereich von 19,0 - 20,7 MPa (2750 - 3000 psig) und die Temperatur im Bereich von 329°C - 371°C (625°F - 700°F) liegt.

8. Verfahren nach einem der Ansprüche 2 bis 7, bei dem die letzte, weniger starke Hydrierung in Gegenwart eines Platinreformierungskatalysators durchgeführt wird.

9. Verfahren nach Anspruch 8, bei dem die letzte, weniger starke Hydrierung bei einem Wasserstoffpartialdruck im Bereich von 17,2 - 20,7 MPa (2500 - 3000 psig) und einer Temperatur im Bereich von 232°C - 288°C (450°F - 550°F) durchgeführt wird.

Revendications

1. Procédé de préparation d'une huile minérale blanche de qualité alimentaire à partir d'un substrat naphténique sans extraction par un solvant et sans traitement avec un acide, en continu, dans lequel le substrat est soumis à une pluralité d'étapes d'hydrotraitement en série, caractérisé en ce que :
(i) on soumet ledit substrat à trois opérations d'hydrogénation ;
(ii) on effectue la première opération d'hydrogénation à une température comprise entre 288°C et 399°C (entre 550°F et 750°F) et à une pression partielle d'hydrogène d'au moins 8,2 MPa au manomètre (1200 psig), mais moins de 13,7 MPa au manomètre (2000 psig) ;
(iii) le flux d'amenée à la deuxième opération comprend le produit liquide provenant de la première opération ; et
(iv) le flux d'amenée à la troisième opération comprend le produit liquide provenant de la deuxième opération.

2. Procédé tel que revendiqué dans la revendication 1, comprenant les étapes consistant à :
(a) réduire la teneur en composés aromatiques du flux d'amenée d'environ 50 % lors d'une première opération d'hydrogénation ;
(b) séparer les constituants gazeux du produit liquide hydrogéné de l'opération (a) ;
(c) réduire la teneur en carbures aromatiques du produit liquide de l'opération (a), après avoir séparé les constituants gazeux de celui-ci, à environ 1 %, en soumettant ledit produit à une deuxième opération d'hydrogénation ;
(d) séparer les constituants gazeux du produit d'hydrogénation de l'opération (c) ; et
(e) produire l'huile minérale blanche de qualité alimentaire ne contenant qu'une trace de composés aromatiques, en soumettant le produit liquide de l'étape (c), après avoir sé-

paré les constituants gazeux de celui-ci, à une opération d'hydrogénation finale dans des conditions moins rigoureuses que celles de l'opération (a) et de l'opération (b).

3. Procédé tel que revendiqué dans la revendication 1 ou 2, dans lequel le flux d'amenée est un distillat naphténique ou cycloparaffinique contenant une concentration de carbures aromatiques valant de 15 à 25 % en poids.

4. Procédé selon la revendication 3, dans lequel on effectue ladite première hydrogénation avec un catalyseur de nickel-molybdène, et lesdits constituants gazeux dudit produit hydrogéné comprennent du sulfure d'hydrogène et de l'ammoniac, que l'on sépare par rectification.

5. Procédé selon la revendication 3 ou 4, dans lequel on effectue ladite première hydrogénation à une pression partielle d'hydrogène comprise entre 10,3 et 12,4 MPa (1500 - 1800 PSIG), et à une température comprise entre 343°C et 371°C (650 - 700°F).

6. Procédé selon l'une quelconque des revendications 2 à 5, dans lequel on effectue ladite deuxième hydrogénation avec un catalyseur de nickel-molybdène, et lesdits constituants gazeux dudit deuxième produit hydrogéné comprennent du sulfure d'hydrogène et de l'ammoniac, que l'on sépare par rectification.

7. Procédé selon la revendication 6, dans lequel ladite pression partielle d'hydrogène est comprise entre 19,0 et 20,7 MPa (2750 - 3000 PSIG), et où ladite température est comprise entre 329 et 371°C (625 - 700°F).

8. Procédé selon l'une quelconque des revendications 2 à 7, dans lequel on effectue ladite hydrogénation finale moins rigoureuse en présence d'un catalyseur de reformation du platine.

9. Procédé selon la revendication 8, dans lequel on effectue ladite hydrogénation finale moins rigoureuse à une pression partielle d'hydrogène comprise entre 17,2 et 20,7 MPa (2500 - 3000 PSIG) et à une température comprise entre 232 et 288°C (450 - 550°F).

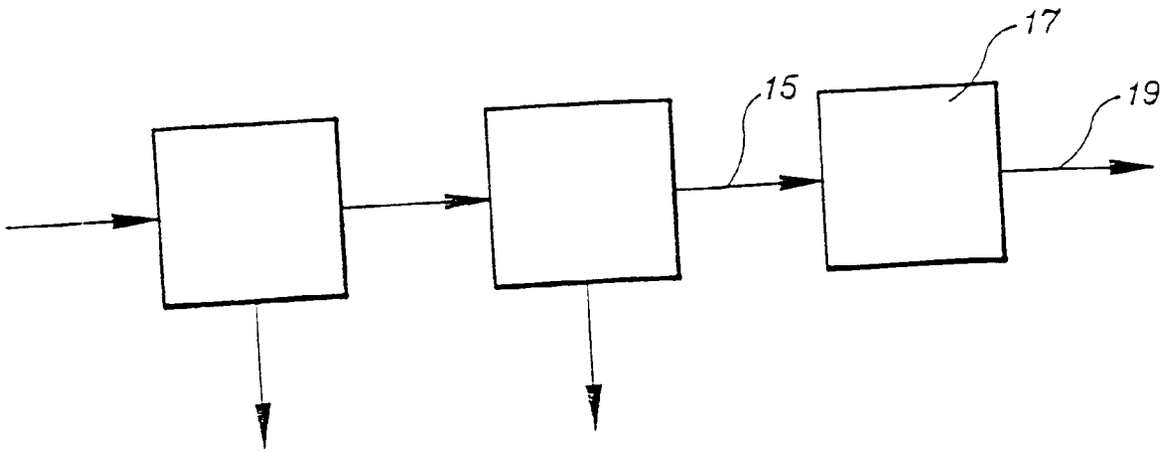

FIG. 1.

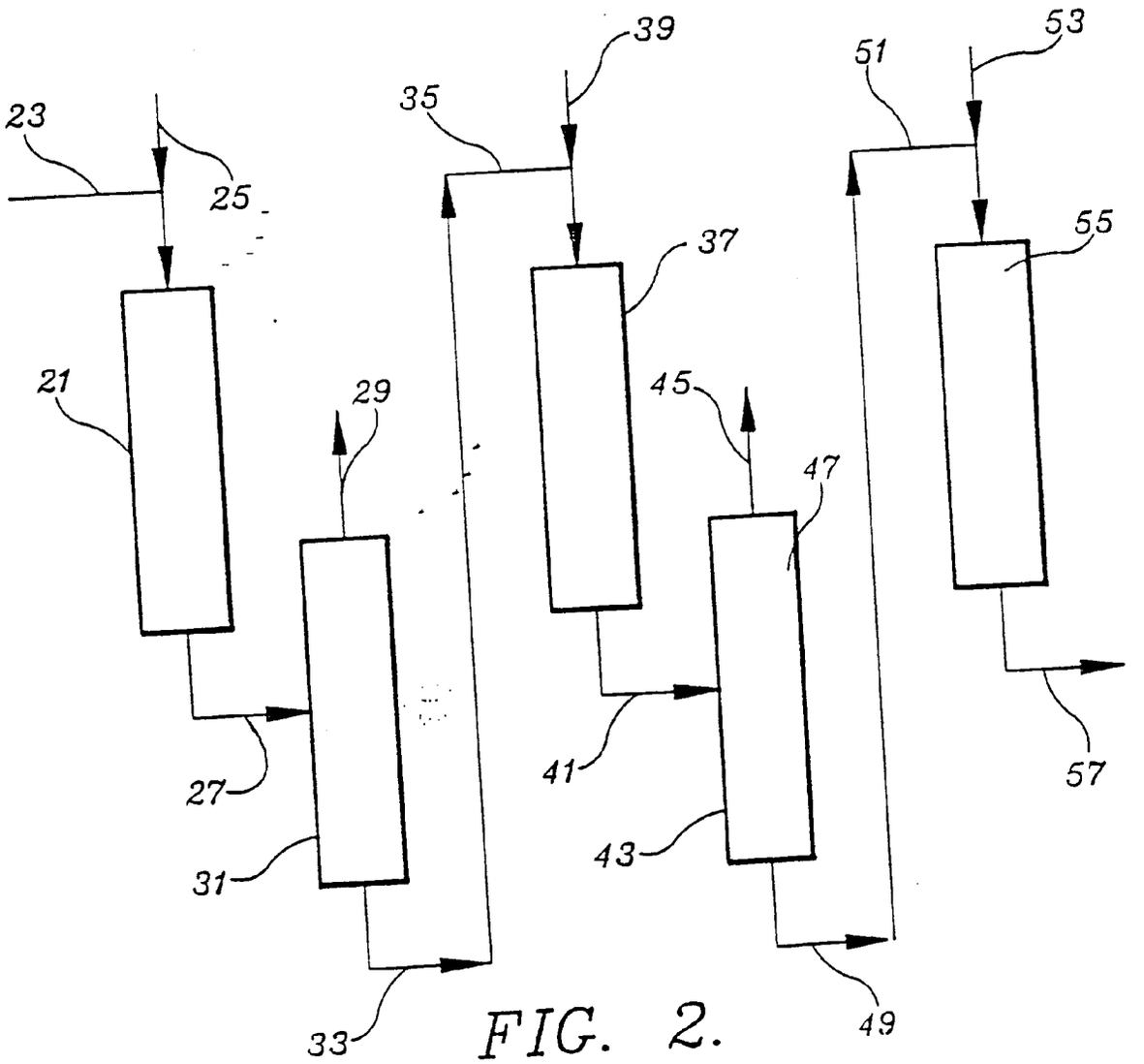

FIG. 2.