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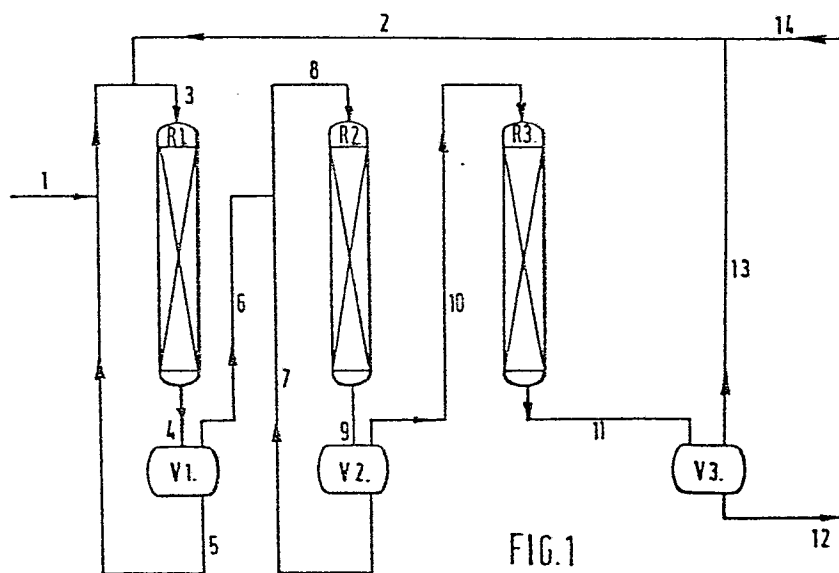
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54 Process for selective hydrogenation of dienes in pyrolysis gasoline.

57 A process for the selective hydrogenation of dienes in pyrolysis gasoline which comprises catalytic hydrogenation of the pyrolysis gasoline in at least three consecutive reactors (R₁, R₂ and R₃) in at least two of the said consecutive reactors recirculating part of the hydrocarbon mixture emerging from a reactor over that reactor, (5 and 7) no recirculation of the hydrocarbon mixture emerging from the last of the consecutive reactor (R₃) being carried out over that reactor.

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PROCESS FOR SELECTIVE HYDROGENATION OF DIENES IN PYROLYSIS
GASOLINE

This invention relates to a process for the selective hydrogenation of dienes in pyrolysis gasoline.

As will be known, pyrolysis gasoline is obtained as a by-product in the preparation of ethene and/or propene by means of
5 high-temperature pyrolysis (e.g. cracking in the presence of steam) of gaseous or liquid hydrocarbons, such as naphtha or gas oil.

Pyrolysis gasolines on the one hand are extremely unstable owing to the presence of a relatively high proportion of highly
10 olefinically unsaturated hydrocarbons, and on the other hand contain aromatic compounds and alkenes having a high octane number which are particularly valuable and are in themselves useful as stable motor gasoline components.

In order to obtain a stable gasoline with high octane
15 number from a pyrolysis gasoline the highly olefinically unsaturated compounds, which mainly consist of dienes, for example those of the cyclopentadiene type, have to be removed therefrom. This removal may be achieved by partial hydrogenation of the dienes to mono-olefins. Because the hydrogenation of mono-
20 olefins in general leads to a reduction in octane number, such a hydrogenation is to be avoided as much as possible. Moreover, in doing so the hydrogen consumption is kept to a desired low level.

It is known to hydrogenate dienes present in pyrolysis gasolines selectively with the aid of catalysts with hydrogenating activity such as supported catalysts comprising a metal of Group VI and/or Group VIII of the Periodic System of Elements.

In order to convert a high proportion of the dienes originally present without incurring unacceptably high process temperatures, it has been proposed to recycle part of the product obtained after the selective hydrogenation to the reactor in which the selective hydrogenation is being carried out. However, it is felt as a drawback that during such a process an appreciable amount of mono-olefins is also hydrogenated, which leads to an unattractively high hydrogen consumption.

The invention provides a solution for this problem by using at least three consecutive reactors and a specific recirculation pattern.

Accordingly, the invention provides a process for the selective hydrogenation of dienes in pyrolysis gasoline which comprises catalytic hydrogenation of the pyrolysis gasoline in at least three consecutive reactors, in at least two of the said consecutive reactors recirculating part of the hydrocarbon mixture emerging from a reactor over that reactor, no recirculation of the hydrocarbon mixture emerging from the last of the consecutive reactors being carried out over that reactor.

It is to be understood that recirculating part of the hydrocarbon mixture emerging from a reactor over that reactor, stands for the direct recirculation of the said hydrocarbon mixture, no further hydrogenation thereof being carried out in any subsequent reactor before the recirculation.

It is essential that in at least two of the consecutive reactors recirculation of part of the hydrocarbon mixture emerging from each of these reactors over the relevant reactor is carried out, because in case two consecutive reactors are

used and the recirculation is carried out over one reactor only the amount of dienes still present in the ultimate product of the process cannot be brought to an acceptable low level without extensive hydrogenation of the mono-olefins, the latter giving
5 rise to an undesired high level of hydrogen consumption.

Preferably, the number of consecutive reactors is three. More reactors may be used, and the recirculation as described may be carried out over more than two reactors, but in general the advantage to be achieved (less hydrogenation of mono-olefins
10 at a preset amount of dienes in the ultimate product) does not compensate for the drawbacks which consist of building and handling of an extra reactor.

The catalyst with hydrogenating activity to be used in the reactors very suitably consists of a support comprising one or
15 more metals of Group VIB and/or Group VIII of the Periodic System of Elements and/or compounds of these metals. The support very suitably consists of alumina, silica or silica alumina. Catalysts comprising platinum or palladium are very suitable. The most preferred catalyst comprises partially sulphided nickel on
20 alumina as a support.

The catalyst very suitably is in the form of one or more fixed beds in the reactors, and the catalytic hydrogenations are preferably carried out by passing a mixture of liquid and hydrogen-containing gas in downflow over the catalyst according to the trickle flow technique. In this technique, the starting
25 hydrocarbon oil which is present partly in the liquid phase and partly in the vapour phase is allowed to flow downward in the presence of hydrogen or of a hydrogen-containing gas over a catalyst in the form of a fixed bed, the unvaporized part of the starting material flowing over the catalyst particles in
30 the form of a thin liquid layer.

The recirculation ratios over the respective reactors are to be chosen such that in each of these reactors the ratio of the dienes hydrogenated to mono-olefins on the one hand and

the mono-olefins hydrogenated to paraffins on the other hand, is high because in this way the overall hydrogen consumption is kept low. It has been found that the weight ratio of the hydrocarbon mixture recirculated to the first reactor and the
5 pyrolysis gasoline fed thereto very suitably is from 5 to 15, in particular from 9 to 11. The preferred weight ratio of the hydrocarbon mixture recirculated to the second reactor and the hydrocarbon mixture emerging from the first reactor which is fed to the second reactor, has been found to be from 2 to 4.

10 No recirculation is to be used in the final reactor of the consecutive reactors, because the amount of dienes still present in the hydrocarbon mixture fed to that reactor is so low that at relatively high space velocity hydrogenation thereof to mono-olefins can lead to the desired concentration of dienes
15 in the effluent without undue hydrogenation of mono-olefins to paraffins.

The hydrogen to be employed in the catalytic hydrogenation may be pure or in the form of a hydrogen-containing gas. The gases employed should preferably contain more than 50% by volume
20 of hydrogen. Very suitable are, for example, the hydrogen-containing gases obtained in the catalytic reforming or steam-reforming of gasoline fractions, and mixtures of hydrogen and light hydrocarbons. Any excess of hydrogen-containing gas is advantageously recycled, possibly after the previous removal of
25 undesired components therefrom.

The catalytic hydrogenations are very suitably carried out at the following conditions in the reactors: a temperature in the range from 50-250°C, preferably 50-150°C, a total pressure in the range from 10-80 bar a and a hydrogen partial pressure in
30 the range from 5-60 bar a.

The liquid hourly space velocity of the hydrocarbon mixture which is fed to a reactor for the first time (e.g., the fresh feed fed to the first reactor or that part of the effluent of a

reactor which is fed to the next reactor) may vary for any reactor. In order to calculate the space velocity of the mixture obtained after combination of the recycle liquid and the hydrocarbon mixture which is fed to a particular reactor for the first time, the space velocity of the last-mentioned hydrocarbon mixture is to be multiplied by the recirculation ratio used for that reactor. Very suitably the liquid hourly space velocities of the mixtures obtained after combination of the recycle liquid and the hydrocarbon mixture which is fed to a particular reactor for the first time, are between 5 and 50 and preferably between 10 and 20 kg mixture per litre catalyst per hour. At lower space velocities the extent of heat release of the hydrogenation reaction may be such that temperature control becomes difficult if not impossible.

The space velocities of the hydrocarbon mixtures fed for the first time to a particular reactor to which recycling is taking place, will in general be less than 5 kg per litre catalyst per hour.

In the last reactor, the feed of which only contains relatively low amounts of dienes, the space velocity very suitably ranges from 2-20 and preferably from 5-10 kg feed per litre catalyst per hour.

The ratio of fresh gas to fresh feed very suitably is from 50-500 Nl gas per kg feed, and the ratio of recycle gas to fresh feed from 200-500 Nl gas per kg feed.

The accompanying figure 1 represents a simplified flow diagram of a suitable embodiment of the process according to the invention. In this figure various auxiliary devices, such as pumps, cocks, valves, control valves, etc. have been omitted.

A pyrolysis gasoline is fed in via line 1, and after mixing with a hydrogen-containing gas supplied via line 2, introduced into reactor R1 via line 3. Reactor R1 contains one or more fixed beds of catalyst. The effluent of R1 is led via line 4 to separation vessel V1 in which gas and liquid (the latter

consisting substantially of hydrocarbons) are separated. Part of the liquid is transported via line 5, mixed with pyrolysis gasoline from line 1 and recirculated to R1 via line 3. The remainder of the liquid in V1 and the gas are forwarded via line 6, mixed with a liquid stream emerging from separating vessel V2 via line 7, and fed to reactor R2 via line 8. Reactor R2 contains one or more fixed beds of catalyst. The effluent from reactor R2 is forwarded via line 9 to separation vessel V2, in which vessel liquid and gas are separated. Part of the liquid is recycled via line 7 as described, and the remainder of the liquid and the gas from V2 are fed to reactor R3 via line 10. The effluent from reactor R3, which reactor contains one or more fixed beds of catalyst, is led to separation vessel V3 via line 11. In V3 gas and liquid are separated. The liquid is removed via line 12 as the final product of the process, the gas from V3 is (if desired after purification) forwarded via line 13 to line 2, in which line fresh hydrogen-containing gas is fed via line 14.

EXAMPLE

The process was carried out according to the flow scheme given in Figure I.

Fresh feed in line 1 consisted of a pyrolysis gasoline which contained 60.2%w dienes and 20.0%w mono-olefins. This feed was added at a space velocity of 1.48 kg/l catalyst in R1/hour. The catalyst in all reactors consisted of partially sulphided nickel on alumina, the amount of nickel being 10.7%w on carrier. The inlet temperature of R1 was 63°C, the temperature at the outlet of this reactor was 90°C, the average pressure in R1 was 62.5 bar a (H_2 partial pressure 45.4 bar a). The effluent of R1 was separated in V1 at 90°C, and 10 times the amount of liquid fed via line 1 was recycled from V1 via line 5 (recycle ratio 10). This recycle liquid contained 18.4%w dienes. The remainder of the liquid and the gas in V1 were led

via line 6 at a space velocity of 4.13 kg/l catalyst in R2/hour to reactor R2. The inlet temperature of R2 was 83°C, the outlet temperature 104°C and the average pressure 61.5 bar a (H_2 partial pressure 40.6 bar a). The effluent from R2 was separated at
5 104°C in separator V2 in liquid and gas, and 3.2 times the amount of liquid fed via line 6 was recycled from V2 via line 7 to R2 (recycle ratio 3.2). The recycle liquid contained 5.8%w dienes. The remainder of the liquid and gas in V2 were forwarded via
10 line 10 to reactor R3 at a space velocity of 6.89 kg/l catalyst in R3/hour. The inlet temperature of R3 was 90°C, the outlet temperature 123°C and the average total pressure 59.5 bar a (H_2 partial pressure 34.4 bar a). The effluent of R3 was separated in V3, and the liquid removed as final product of the process via line 12. This product contained 0.5%w diolefins
15 and 72.7%w mono-olefins. The gas from V3 was recycled via line 13 and mixed with fresh hydrogen-containing gas, the latter containing 94.1 mol.% hydrogen, 4.6 mol.% methane, 1.0 mol.% nitrogen and 0.3 mol.% water. Fresh gas was supplied via line
20 line 13 amounted to 300 Nl/kg fresh feed and contained 75.0 mol.% hydrogen, 11.8 mol.% methane, 6.2 mol.% nitrogen, 2.0 mol.% water, the remainder consisting of hydrocarbons with at most 6 carbon atoms. The amount of hydrogen consumed per kg feed for undesired mono-olefin saturation was 0.002 kg.

25 Comparative Example

The process was carried out according to the flow scheme given in Figure 2.

Fresh feed in line 1 consisted of a pyrolysis gasoline which contained 60.2%w dienes and 20.0%w mono-olefins. This feed was
30 added at a space velocity of 0.42 kg/l catalyst in R1/hour. The catalyst in both reactors consisted of partially sulphided nickel on alumina, the amount of nickel being 10.7%w on carrier. The inlet temperature of R1 was 63°C, the temperature at the outlet

of this reactor was 90°C, the average pressure in R1 was 62.5 bar a (H_2 partial pressure of 40 bar a at reactor outlet. The effluent of R1 was separated in V1 at 90°C, and 13 times the amount of liquid fed via line 1 was recycled from V1 via line 5 (recycle ratio 13). This recycle liquid contained 5.8%w dienes. The remainder of the liquid and the gas in V1 were forwarded via line 6 to reactor R2 at a space velocity of 6.89 kg/l catalyst in R2/hour. The inlet temperature of R2 was 90°C, the outlet temperature 123°C and the average total pressure 59.5 bar a (H_2 partial pressure 32 bar a at reactor outlet). The effluent of R2 was separated in V2 and the liquid removed as final product of the process via line 8. This product contained 0.5%w diolefins and 69.9%w mono-olefins. The gas from V2 was recycled via line 9 and mixed with fresh hydrogen-containing gas, containing 94.1 mol.% hydrogen, 4.6 mol.% methane, 1.0 mol.% nitrogen and 0.3 mol.% water. Fresh gas was supplied via line 10 in an amount of 244 Nl/kg fresh feed. Recycle gas via line 9 amounted to 300 Nl/kg fresh feed and contained 73.8 mol.% hydrogen, 12.8 mol.% methane, 6.7 mol.% nitrogen, 2.3 mol.% water, the remainder consisting of hydrocarbons with at most 6 carbon atoms. The amount of hydrogen consumed per kg of feed for undesired mono-olefin saturation was 0.003 kg, which is 50% higher than in the Example according to the invention.

C L A I M S

1. A process for the selective hydrogenation of dienes in
pyrolysis gasoline which comprises catalytic hydrogenation of
the pyrolysis gasoline in at least three consecutive reactors,
in at least two of the said consecutive reactors recirculating
5 part of the hydrocarbon mixture emerging from a reactor over
that reactor, no recirculation of the hydrocarbon mixture emerging
from the last of the consecutive reactors being carried out over
that reactor.
2. A process as claimed in claim 1, in which the number of
10 consecutive reactors is three.
3. A process as claimed in claim 1 or 2, in which the catalyst
used for the catalytic hydrogenation comprises partially sulphided
nickel on alumina as a support.
4. A process as claimed in any one of the preceding claims, in
15 which the weight ratio of hydrocarbon mixture recirculated to
the first reactor and the pyrolysis gasoline fed thereto is from
5 to 15.
5. A process as claimed in claim 4, in which the said ratio is
from 9 to 11.
- 20 6. A process as claimed in any one of the preceding claims, in
which the weight ratio of the hydrocarbon mixture recirculated to
the second reactor and the hydrocarbon mixture emerging from the
first reactor which is fed to the second reactor is from 2 to 4.
7. A process as claimed in any one of the preceding claims,
25 in which the temperature in the reactors is in the range from
50 to 250°C, the total pressure is in the range from 10 to 80
bar a, and the hydrogen partial pressure is in the range from
5 to 60 bar a.
8. A process as claimed in any one of the preceding claims,
30 in which the catalytic hydrogenation is carried out in down-
flow according to the trickle flow technique.
9. A process as claimed in claim 1, substantially as described,
with special reference to the Example.

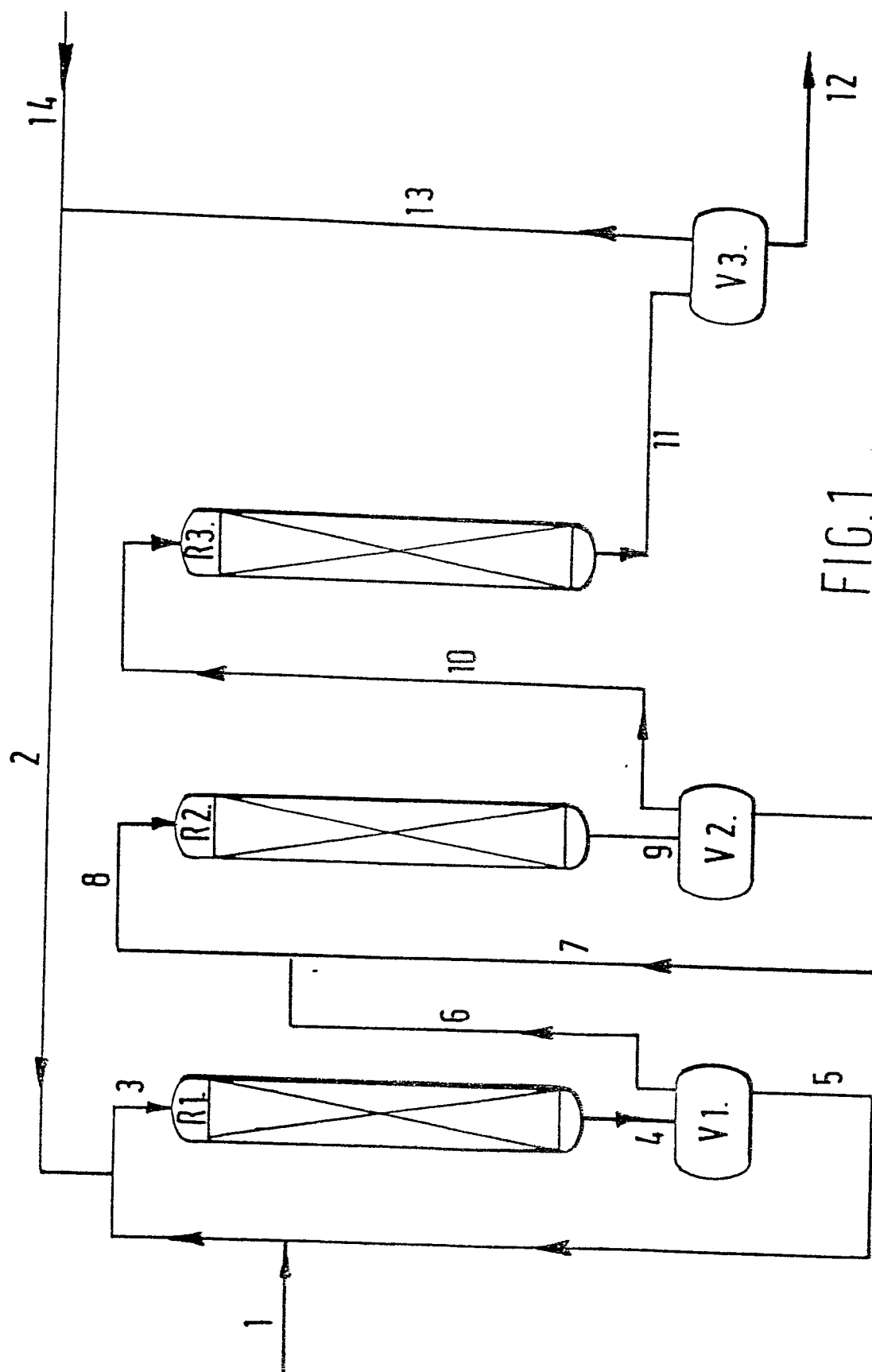


FIG. 1

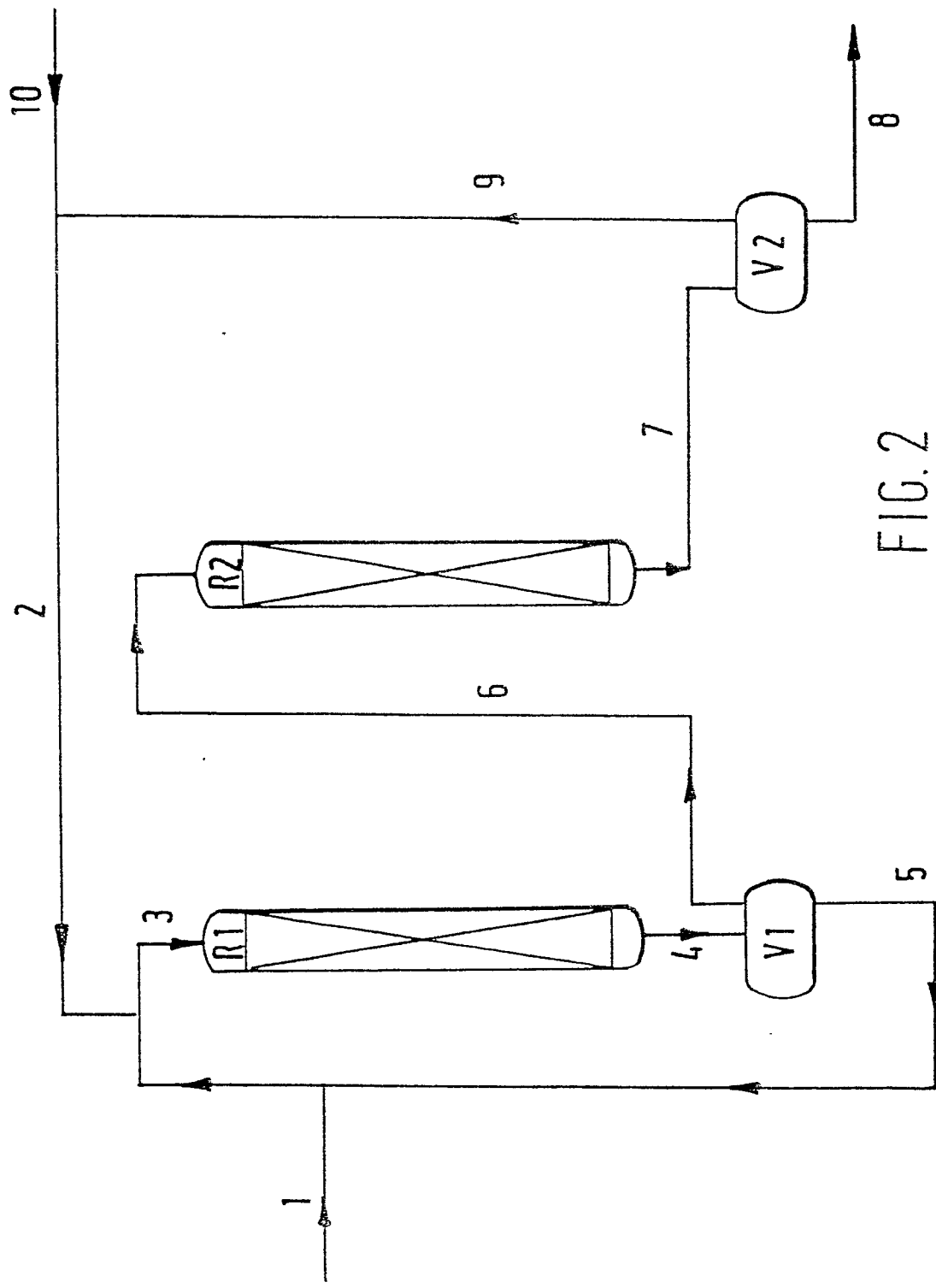


FIG. 2



European Patent
Office

EUROPEAN SEARCH REPORT

0011906
Application number
E 19 20 0716

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	US - A - 3 492 220 (LEMPERT et al.)		C 10 G 65/06
A	FR - A - 1 289 849 (SHELL)		
A	GB - A - 1 210 128 (AIR PRODUCTS AND CHEMICALS)		
A	US - A - 3 470 085 (PARKER)		

			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 10 G 65/06 C 10 G 45/32 45/34 45/36 45/38 45/40
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family. corresponding document
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	04-03-1980	MICHIELS	