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PROCESS FOR THE HYDROCRACKING OF A HYDROCARBONACEOUS FEEDSTOCK

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(57) Claim

1. Process for the hydrocracking of a hydrocarbonaceous feedstock which process comprises contacting the feedstock in a first reaction stage at elevated temperature and pressure in the presence of hydrogen with a first hydrocracking catalyst to obtain a first effluent, separating from the first effluent a gaseous phase and a liquid phase at substantially the same temperature and pressure as prevailing in the first reaction stage, contacting the liquid phase of the first effluent in a second reaction stage at elevated temperature and pressure in the presence of hydrogen with a second hydrocracking catalyst to obtain a second effluent and obtaining at least one desired product by fractionation of the combined gaseous phase and the second effluent.

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Complete Specification for the invention entitled:

Process for the Hydrocracking of a Hydrocarbonaceous
Feedstock

The following statement is a full description of this invention, including the
best method of performing it known to me/us

T 5241

A B S T R A C T

PROCESS FOR THE HYDROCRACKING OF
A HYDROCARBONACEOUS FEEDSTOCK

A hydrocarbonaceous feedstock is hydrocracked by contacting the feedstock in a first reaction stage at elevated temperature and pressure in the presence of hydrogen with a first hydrocracking catalyst to obtain a first effluent, separating from the first effluent a gaseous phase and a liquid phase at substantially the same temperature and pressure as prevailing in the first reaction stage, contacting the liquid phase of the first effluent in a second reaction stage at elevated temperature and pressure in the presence of hydrogen with a second hydrocracking catalyst to obtain a second effluent and obtaining at least one desired product by fractionation of the combined gaseous phase and the second effluent.

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PROCESS FOR THE HYDROCRACKING OF
A HYDROCARBONACEOUS FEEDSTOCK

The present invention relates to a process for the hydrocracking of a hydrocarbonaceous feedstock in which a plurality of reaction stages are employed.

Hydrocracking is a well-established process in
5 which heavy hydrocarbons are contacted in the presence of hydrogen with a hydrocracking catalyst. The temperature and the pressure are relatively high, so that the heavy hydrocarbons are cracked to products with a lower boiling point. Although the process can be
10 carried out in one stage, it has shown to be advantageous to carry out the process in a plurality of stages. In a first stage the feedstock is subjected to denitrogenation, desulphurisation and hydrocracking, and in a second stage most of the hydrocracking
15 reactions occur.

The presence of nitrogen compounds in the feedstock may lead to problems as, generally, hydrocracking catalysts are nitrogen-sensitive and may be deactivated by the nitrogen compounds. Therefore it
20 has been proposed to remove the nitrogen compounds from the effluent of the first stage. The nitrogen compounds, usually comprising ammonia, may be washed out by subjecting the first stage effluent to a treatment with an aqueous solution of, for example, a
25 mineral acid. Apart from the fact that the washing procedure does not always remove any organic nitrogen compounds that remain in the effluent, there is the drawback that the effluent needs to be cooled off significantly in order to obtain a satisfactory removal
30 of the ammonia. Another drawback of the above procedure

resides in the fact that hydrocarbonaceous products that have already been cracked and are valuable desired products, remain in the effluent and can again be cracked in the second stage to yield less desired lighter or even undesired gaseous products.

It has now been found that the above drawbacks are overcome if the first stage effluent is subjected to a separation between gaseous and liquid products at substantially the same temperature and pressure as prevail in the first stage.

It has also been found that the capability of converting the heavier part of the first stage effluent to desired products, whilst avoiding overcracking to unduly light products is improved to the extent that it may permit the operation of the second stage without recycle.

Accordingly, the present invention provides a process for the hydrocracking of a hydrocarbonaceous feedstock which process comprises contacting the feedstock in a first reaction stage at elevated temperature and pressure in the presence of hydrogen with a first hydrocracking catalyst to obtain a first effluent, separating from the first effluent a gaseous phase and a liquid phase at substantially the same temperature and pressure as prevailing in the first reaction stage, contacting the liquid phase of the first effluent in a second reaction stage at elevated temperature and pressure in the presence of hydrogen with a second hydrocracking catalyst to obtain a second effluent and obtaining at least one desired product by fractionation of the combined gaseous phase and second effluent.

By carrying out the separation at substantially the same temperature as prevailing in the first reaction stage there is no need for expensive cooling

and heating processes. Further, due to the relatively high temperature at which the separation is carried out, the solubility of ammonia in the liquid phase will be negligible and cracked products will be entrained with the gaseous phase so that there is no risk of overcracking. The cracked products that are contained in the gaseous phase include valuable middle distillates. Moreover, since there is no risk of overcracking in the second stage, the cracking duty in the first stage may be increased, if that would be desired. Finally, by the removal of the cracked products in the separation stage the quantity of material that is to be processed in the second reaction stage is reduced, so that a smaller reactor may suffice.

In one form of the invention at least one distillate fraction and a residual fraction are obtained by fractionation, and at least a part of the residual fraction is recycled to a reaction stage.

It is preferred to recycle the complete residual fraction. This has the advantage that the complete feedstock is hydrocracked to products with a lower boiling point. This part or the complete residual fraction may be recycled to the first reaction stage. However, since the residual fraction is substantially nitrogen-free and since most of the hydrocracking reactions occur in the second reaction stage, it is preferred to pass the (part of the) residual fraction to the second reaction stage. Thereto it is convenient to combine it with the liquid phase of the first effluent before it is passed to the second reaction stage.

If the conversion in the second reaction stage is sufficiently high, recycle may not be necessary and once-through operation may suffice, thus preventing the

build-up of polycyclic aromatics in the stream which contacts the second stage catalyst. Thus, according to an alternative form of the invention, the desired product or products are obtained by fractionation without recycle.

The choice as to whether to recycle will depend on the desired final product slate. Thus, for example, if high middle distillate selectivity is desired, a combination of lower than theoretically possible conversion perpass together with recycle may provide the optimum yield.

The gaseous phase of the first effluent contains hydrogen and ammonia and generally hydrogen sulphide, and the second effluent comprises at least hydrogen. It is preferred to remove the ammonia and the hydrogen sulphide from the process and to recover the hydrogen which can be recycled to the hydrocracking reactors. Therefore, preferably the gaseous phase of the first effluent and the second effluent are subjected to a removal step of ammonia and hydrogen before being subjected to fractionation. The procedures for the removal of hydrogen, ammonia (and hydrogen sulphide) are known in the art and do not need to be described here.

Hydrocarbonaceous feedstocks that can be used in the present process include gas oils, vacuum gas oils, deasphalted oils, long residues, short residues, catalytically cracked cycle oils, thermally cracked gas oils and syncrudes, optionally originating from tar sands, shale oils, residue upgrading processes or biomass. Combinations of various hydrocarbonaceous feedstock can also be employed. The hydrocarbonaceous feedstock will generally be such that a major part, say over 50 %wt, has a boiling point above 370 °C. The present process is most advantageous when the feedstock

contains nitrogen. Typical nitrogen contents are in the range of up to 5000 ppmw. Nitrogen contents may start from 50 ppmw. The feedstock will generally also comprise sulphur compounds. The sulphur content will usually be in the range from 0.1 to 6 %wt.

The separation of a gaseous and a liquid phase of the first effluent takes place at substantially the same temperature and pressure as prevailing in the first reaction stage. Conveniently this is achieved by refraining from cooling or heating the first effluent. In one embodiment the effluent is passed to a separate separation vessel, suitably a high temperature, high pressure interstage flash vessel arranged at or near the outlet of the first reaction stage. However, this separation vessel may consist of any suitable device known in the art for the separation of a gas and a liquid. Advantageously, the separation vessel is a settling vessel from which at a lower portion the liquid is withdrawn and from an opening above the liquid level the gas is withdrawn. In an alternative embodiment, the first reaction stage and the separation are carried out in the same reaction vessel. This can be achieved by the creation of a settling area in the bottom part of the reaction vessel, from which the gaseous phase and the liquid phase are withdrawn via different openings. This embodiment entails the advantage that no separate separation vessel is needed.

The temperature and the pressure of the separation are substantially the same as those prevailing in the first reaction stage. It will be appreciated that minor fluctuations in the reaction conditions in the first reaction stage may occur. The temperature and the pressure in the separation are then preferably substantially the same as those prevailing in the exit part of the first reaction zone. These conditions

suitably include a temperature of 320 to 450 °C and a pressure of 50 to 250 bar. Preferably, the temperature is from 375 to 425 °C and the pressure is from 75 to 150 bar.

5 As to the process conditions in the first reaction stage it is clear that the temperature and pressure will also conveniently be from 320 to 450 °C and from 50 to 250 bar, respectively. More preferably, the temperature and pressure are from 375 to 425 °C and 75
10 to 150 bar. The hydrogen/oil ratio in the first reaction stage is suitably from 500 to 5000 Nl/kg, more preferably from 750 to 2500 Nl/kg, and the space velocity from 0.1 to 10 kg/l/h, more preferably from 0.2 to 5 kg/l/h.

15 The catalyst in the first stage is preferably a hydrocracking catalyst which also has hydrodenitrogenation activity. Suitable catalysts include a refractory oxide in combination with a group 8 and/or group 6b metal or component thereof. Suitable
20 refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and clays. Preferably the catalyst is a alumina-based catalyst with a group 8 and/or group 6b metal or component thereof.

25 The catalytically active metal from groups 8 and 6b are preferably selected from cobalt, nickel, platinum, palladium, tungsten and molybdenum. Preferably non-noble metal mixtures are used, such as Ni-W, Ni-Mo, Co-Mo and Co-W. The catalyst may further
30 contain phosphorus and/or fluorine to boost its activity. When the catalytically active metals are non-noble they are preferably present on the first hydrocracking catalyst in an amount of 1 to 16 %wt of a group 8 metal and/or from 6 to 24 %wt of a group 6b
35 metal, the weight percentages being based on the total

catalyst. Noble metals are suitably present in a lower amount, e.g. from 0.2 to 2 %wt. Especially when the catalytically active metals are non-noble they are preferably present in their oxidic or even more preferred in their sulphidic form. The preparation of the first hydrocracking catalyst is known in the art.

The second hydrocracking catalyst is preferably different from the first hydrocracking catalyst. The second hydrocracking catalyst may be sensitive to nitrogen compounds. Suitable catalysts include hydrocracking catalysts based on silica-alumina and zeolites. Silica-alumina-based catalysts which tend to be highly nitrogen-sensitive, can be used because of the efficient ammonia removal in the interstage separation. Since zeolitic hydrocracking catalysts tend to be more active, they are especially preferred. Suitable zeolitic catalysts comprise a faujasite-type zeolite, in particular zeolite Y. The silica/alumina molar ratio in such zeolites may vary from 4 to 25, in particular from 6 to 15. The unit cell size of zeolite Y may vary from 2.419 to 2.475 nm, in particular from 2.425 to 2.460 nm. Apart from the zeolite the second hydrocracking catalyst conveniently comprises further catalytically active metals and at least one binder. The binder is suitably selected from silica, alumina, thoria, titania, silica-alumina, zirconia, magnesia and mixtures thereof. In particular alumina is preferred, optionally in combination with silica-alumina.

The catalytically active components on the second hydrocracking catalyst are the same as those on the first hydrocracking catalyst, i.e. a group 8 and/or a group 6b metal or compound thereof. Nickel, cobalt, platinum, palladium, tungsten and molybdenum are preferred. The non-noble metals are preferably in their oxidic or sulphidic form. The amounts of the metals are

preferably from 2 to 25 %wt of a group 6b metal, from 1 to 16 %wt of a group 8 metal when the group 8 metal is not noble and from 0.2 to 2 %wt of a noble group 8 metal, all percentages being based on total catalyst.

5 The process conditions prevailing in the second reaction stage are preferably a temperature from 300 to 425 °C, a pressure from 50 to 250 bar, a space velocity from 0.1 to 10 kg/l/h, and a hydrogen/oil ratio of 250 to 5000 Nl/kg.

10 The process will be further illustrated by means of the following Figures and the following Example. For the sake of simplicity various types of equipment that is not essential to the invention, are not shown.

15 Figure 1 shows one embodiment of the present process in which use is made of a separate separation vessel.

Figure 2 shows an alternative embodiment in which no separation vessel is needed.

20 In Figure 1 a first hydrocracking reactor 1 is shown which contains one or more catalyst beds. In the Figure one catalyst bed 13 is shown, comprising a first hydrocracking catalyst, e.g. an alumina-based catalyst loaded with nickel and molybdenum. A hydrocarbonaceous feedstock is passed through a line 11 and mixed with a
25 hydrogen-containing gas supplied via a line 12. The mixture is passed through the catalyst bed(s) and a first effluent is withdrawn at the bottom of the first reactor via a line 14. The first effluent is passed to a separation vessel 3 which operates at substantially
30 the same temperature and pressure as used in the reactor 1. In the separation vessel 3 a gaseous phase is separated from a liquid phase. The liquid phase is withdrawn via a line 16 and is subsequently mixed with a residual fraction supplied via a line 17a. The
35 mixture is then passed to a second hydrocracking

reactor 2 via the line 17 after having been mixed with a hydrogen-containing gas supplied via a line 18. The second hydrocracking reactor 2 contains one or more catalyst beds, here indicated as catalyst bed 19. The catalyst in the second reactor 2 is advantageously an amorphous silica-alumina carrier loaded with nickel/tungsten or nickel/molybdenum or a zeolite Y-containing carrier loaded with nickel/tungsten or nickel/molybdenum. In the hydrocracking reactor 2 the mixture from the line 17 is hydrocracked and a second effluent is discharged via a line 20, where it is mixed with the gaseous phase of the first effluent from the line 15. The resulting mixture is passed to a separation section 5 where in several stages hydrogen is recovered from the second effluent, ammonia and hydrogen sulphide that have been formed during the process are removed and a hydrocarbonaceous product is obtained. The hydrogen is recovered via a line 22, where it is mixed with make-up hydrogen supplied via a line 23. The line 22 then splits into the lines 12 and 18 that provide the hydrogen for the reactors 1 and 2, respectively. The waste ammonia and hydrogen sulphide are discharged via a line 21 and can be subjected to gas purification and sulphur recovery. The hydrocarbonaceous product is passed via a line 24 to a fractionation section, here indicated as a fractionator 4, where it is divided into gaseous and liquid distillate fractions that are recovered via lines 25, 25a, 25b and 25c. The residue of the fractionation is withdrawn via the line 17a. It will be apparent that the cut point for the residual fraction can be arranged at will in accordance with the desired products. As shown, line 17a recycles the residual fraction to the line 17. Recycle may not be necessary if once-through operation results in an acceptable product slate.

In the embodiment of Figure 2 the separation vessel has been deleted. The numbering of equipment in Figure 2 is the same as in Figure 1 when reference is made to corresponding equipment. The hydrocarbonaceous feedstock is mixed with a hydrogen-containing gas and passed to the first hydrocracking reactor 1. The reactor 1 is provided with a settling area 30. When the feedstock has passed the catalyst bed(s) 13, a first effluent enters the settling zone 30 and a separation occurs between a gaseous and liquid phase. The liquid phase is withdrawn from the reactor at the bottom of the reactor 1 via a line 32, and the gaseous phase is withdrawn from the reactor 1 at a higher position via a line 31. The liquid phase in line 32 is mixed with the residual fraction from the fractionator 4 in line 17a and is subsequently cracked in the second hydrocracking reactor 2. The second effluent is withdrawn via the line 20, mixed with the gaseous phase of the first effluent from line 31 and the resulting mixture is worked up as described for the embodiment of Figure 1.

EXAMPLE

A feedstock A, derived from a synthetic crude, originating from the upgrading of Athabasca tarsands (syncrude, Fort McMurray, Canada), and having the properties given in Table 1 below, was subjected to first stage hydrotreating over a commercially available catalyst containing nickel (3% by weight), molybdenum (13% by weight) and phosphorus (3.2% by weight) on alumina, which catalyst had been diluted with an equal volume of 0.2 mm SiC and calcined and sulphided prior to use. The hydrotreating was carried out at an inlet pressure of 125 bar, a space velocity of 1 kg/l/h and a hydrogen/oil ratio of 800 to 900 nl/kg. The temperature was adjusted to maintain a conversion of 338 °C⁺ materials of 21-22% and was in the range of 380 to 383

°C. The total first stage liquid products were recovered.

For use in an Experiment 1 to illustrate the invention, a portion of the first stage liquid product
5 was subjected to a fractionation to produce a top and bottom fraction. The bottom fraction, feedstock B, had the properties given in Table 1 and was selected to represent the calculated feedstock constitution
10 obtained by subjecting the product of the first stage hydrotreating to a gas/liquid separation at substantially the same high temperature and pressure as prevailing at the outlet of the first stage, i.e. 395
°C and 140 bar. Dosages of dimethyl disulphide and
15 t-butylamine were incorporated in feedstock B to adjust the level of H_2S and NH_3 to that which would be present in a liquid effluent obtained by such high temperature and pressure separation.

For use in a comparative Experiment 2, a portion
20 of the entire first stage liquid product was used, after dosing with dimethyl disulphide and t-butylamine (to simulate the H_2S and NH_3 produced in the first stage), as feedstock C, the properties of which are given in Table 1.

TABLE 1

Feedstock	A	B	C
Density (15 °C), g/cm ³	0.910	0.905	0.882
C, %w	87.8	87.3	86.9
H, %w	11.9	12.5	12.9
S, ppmw	2300	1940	1360
N, ppmw	750	60	30
I.B.P., °C	172	251	101
10/20	214/246	300/329	194/221
30/40	276/301	344/350	248/274
50/60	327/354	373/390	297/323
70/80	382/415	410/434	350/383
F.B.P.	533	542	522

Feedstocks B and C were separately subjected to once-through hydrocracking in a second stage over a zeolitic catalyst comprising 8.4 %w W and 2.5 %w Ni. The zeolitic catalyst carrier consisted of 10 %w alumina and 90 %w zeolite Y having a unit cell size of 2.433 nm. The catalyst was diluted with an equal volume of 0.2 mm SiC, calcined and sulphided prior to use. The hydrocracking was carried out at conditions selected to give the desired conversion of 338 °C⁺ materials. For an overall conversion in the first and second stages of about 99%, the second stage was operated at an inlet pressure of 125 bar, a space velocity of 0.46 to 0.50 kg/l/hr, a temperature of 378 to 379 °C and a hydrogen/oil ratio of 940 to 1025 nl/kg.

The results for 99% overall conversion for Experiment 1 and comparative Experiment 2 are given in Table 2 below.

TABLE 2

Yield (%w on feed)	Experiment 1	Experiment 2
C ₄ ⁻	6.8	11.7
C ₅ -190 °C	52.8	78.8
190-288 °C	38.3	10.6
288-338 °C	4.3	0.9

It will be appreciated from the above results that the experiment illustrating the invention (Experiment 1) gives a reduced gas make and an increased proportion of middle distillates.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for the hydrocracking of a hydrocarbonaceous feedstock which process comprises contacting the feedstock in a first reaction stage at elevated temperature and pressure in the presence of hydrogen with a first hydrocracking catalyst to obtain a first effluent, separating from the first effluent a gaseous phase and a liquid phase at substantially the same temperature and pressure as prevailing in the first reaction stage, contacting the liquid phase of the first effluent in a second reaction stage at elevated temperature and pressure in the presence of hydrogen with a second hydrocracking catalyst to obtain a second effluent and obtaining at least one desired product by fractionation of the combined gaseous phase and the second effluent.
2. Process according to claim 1, in which at least one distillate fraction and a residual fraction are obtained by fractionation, and at least part of the residual fraction is recycled to a reaction stage.
3. Process according to claim 2, in which the complete residual fraction is recycled to a reaction stage.
4. Process according to claim 2 or 3, in which the (part of the) residual fraction that is recycled, is combined with the liquid phase of the first effluent and is passed to the second reaction stage.
5. Process according to claim 1, in which the desired product or products are obtained without recycle.
6. Process according to any one of claims 1-5, in which the gaseous phase of the first effluent and the second effluent are subjected to a removal step of

ammonia and hydrogen before being subjected to fractionation.

5 7. Process according to any one of claims 1-6, in which the separation of the first effluent is carried out without heating or cooling the effluent.

8. Process according to any one of claims 1-7, in which the first reaction stage and the separation are carried out in the same reaction vessel.

10 9. Process according to any one of claims 1-8, in which the temperature in the first reaction stage is from 320 to 450 °C and the pressure is from 50 to 250 bar.

15 10. Process according to any one of claims 1-9, in which the hydrogen/oil ratio in the first reaction stage is from 500 to 5000 Nl/kg and the space velocity from 0.1 to 10 kg/l/h.

20 11. Process according to any one of claims 1-10, in which the first hydrocracking catalyst is an alumina-based catalyst comprising a group 8 and/or group 6b metal or a component thereof.

25 12. Process according to any one of claims 1-11, in which in the second reaction stage the prevailing temperature is from 300 to 450 °C, the pressure is from 50 to 250 bar, the space velocity is from 0.1 to 10 kg/l/h and the hydrogen/oil ratio is from 250 to 5000 Nl/kg.

30 13. Process according to any one of claims 1-12, in which the second hydrocracking catalyst is a zeolite-based catalyst comprising a group 8 and/or a group 6b metal or component thereof.

14. Process for the hydrocracking of a hydrocarbonaceous feedstock substantially as hereinbefore described with reference to the Example.

15. Process for the hydrocracking of a hydrocarbonaceous feedstock substantially as hereinbefore described with reference to the accompanying drawings.

16. The product of the process of any one of claims 1 to 15.

DATED this TWENTY-SEVENTH day of JULY 1989
Shell Internationale Research Maatschappij B.V.

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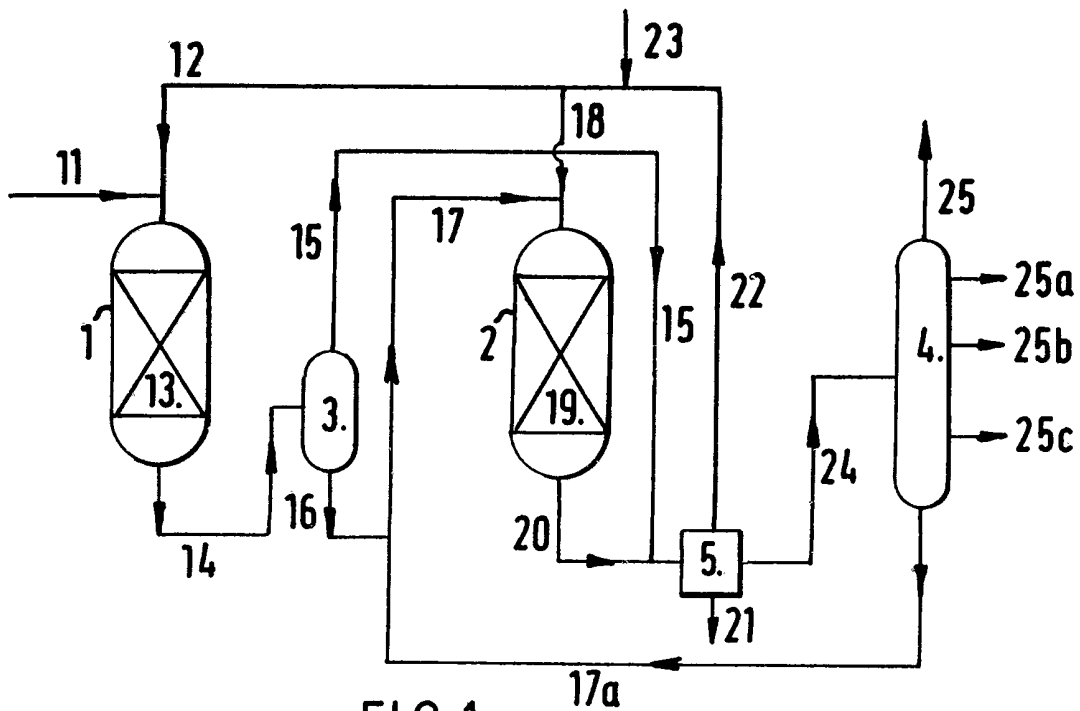


FIG. 1

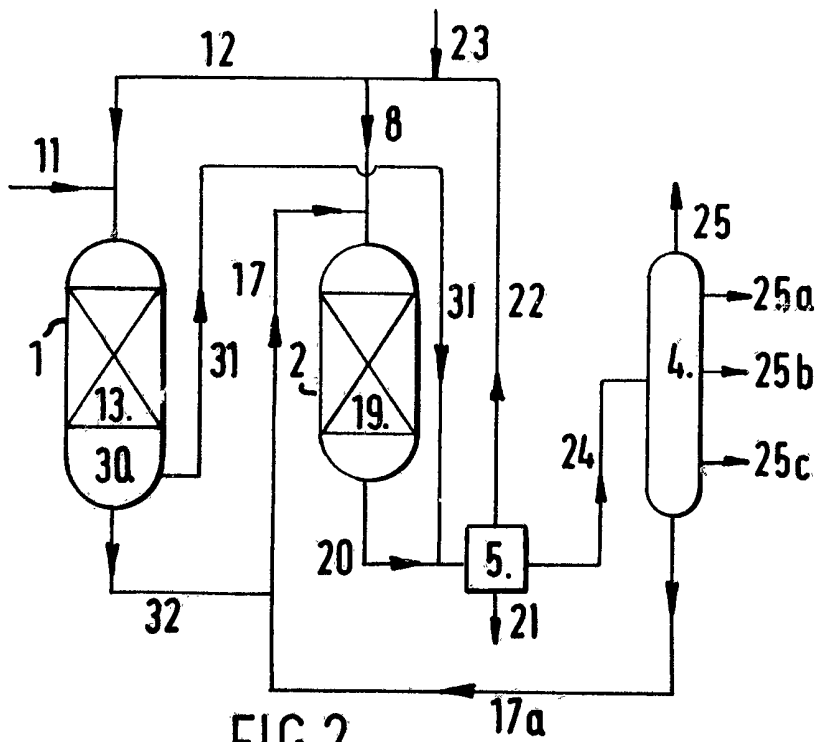


FIG. 2