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(71) Applicant : **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)

(72) Inventor : **Gosselink, Johan Willem**
Badhuisweg 3
1031 CM Amsterdam (NL)
Inventor : **van der Heijden, Anneke**
Badhuisweg 3
1031 CM Amsterdam (NL)
Inventor : **Huizinga, Tom**
Badhuisweg 3
1031 CM Amsterdam (NL)
Inventor : **Schaper, Hennie p/a Shell Int.Petr.Maatsch.B.V.**
department MFTC/54
Carel van Bylandtlaan 30
2596 HR Den Haag (NL)

(54) Process for the conversion of a residual hydrocarbon oil.

(57) Process for the conversion of a residual hydrocarbon oil, preferably a vacuum hydrocarbon oil residue, comprising the following steps :

(a) deasphalting the residual hydrocarbon oil producing an asphaltic fraction and a deasphalted oil (DAO) ;

(b) passing the DAO through a bed of a hydrodemetallisation catalyst in the presence of hydrogen under demetallising conditions, producing an upgraded DAO ; and

(c) blending the upgraded DAO with one or more flashed distillate fractions and subjecting the resulting blend stream to hydrocracking, producing one or more distillate fractions.

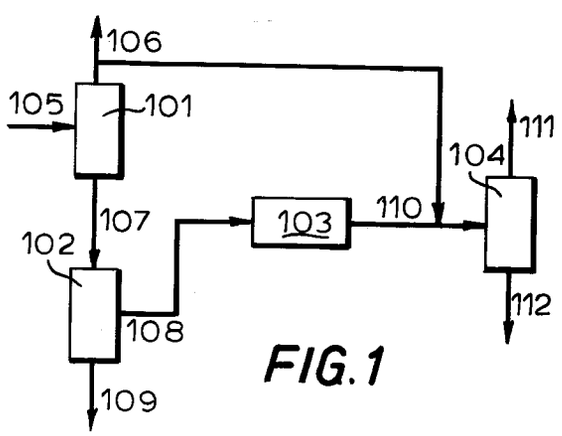

FIG.1

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The present invention relates to a process for the conversion of a residual hydrocarbon oil. More specifically, the present invention relates to a process for the conversion of a residual hydrocarbon oil involving the hydrocracking of upgraded deasphalted oil.

In general, residual hydrocarbon oils, such as those obtained in the distillation of crude oils at atmospheric or reduced pressure, contain considerable amounts of non-distillable compounds having a high molecular weight. Specific examples of such compounds are asphaltenes and metal compounds, in particular vanadium and nickel compounds. If such residual oils are applied as a feed for a catalytic process such as hydrocracking, the metals are deposited on the catalyst particles. As a result of the increasing concentration of in particular nickel and vanadium on the active sites of the catalyst particles, a rapid deactivation of the catalyst occurs. In order to avoid a too rapid deactivation of the catalyst it has therefore been proposed that the metals should be removed from the feed before contacting this feed with the catalyst.

It is well known, e.g. from British patent specifications Nos. 1,438,645; 1,560,590 and 1,560,599, that removal of metals from a hydrocarbon oil feed can be achieved by contacting this feed at elevated temperature and pressure in the presence of hydrogen with a suitable demetallisation catalyst. Demetallisation catalysts are known. They usually consist of oxidic carriers such as alumina, silica or silica-alumina, on which one or more metals or metal compounds having hydrogenation activity are optionally deposited. Metals from Groups VIB and VIII of the Periodic Table of Elements are widely known to be suitable for this purpose. Examples of suitable demetallisation catalysts are disclosed in inter alia U.S. Patents Nos. 3,891,541 and 3,876,523, British patent specifications Nos. 1,438,645; 1,560,590 and 1,560,599, Dutch patent specification No. 7901734, German patent specification No. 2638498 and British patent specifications Nos. 1,548,722 and 1,522,629.

It is generally considered desirable to remove asphaltenes from a hydrocarbon oil feed prior to hydrocracking. However, in that case the asphaltenes removed can no longer contribute to the production of distillates in the hydrocracking treatment and as a result the final yield of distillates is not optimal.

U.S. Patent No. 4,564,439 discloses a two-stage catalytic hydroconversion process, wherein a heavy hydrocarbonaceous feedstock containing more than 100 parts per million by weight (ppmw) of metallic contaminants is first hydrodemetallised and then hydrocracked. Hydrodemetallisation is carried out by mixing the heavy hydrocarbonaceous feedstock, which might be a deasphalted tar or oil, with up to 10% by weight based on feedstock of solid particles which have sufficient catalytic activity to suppress the adverse coke formation and which induce substantial demetallisation. The resulting slurry, suitably in the form of a dispersion, is subsequently introduced into a first-stage hydrothermal zone, wherein hydrogen is introduced as well. The reactant mixture is heated and as a result, demetallisation as well as conversion of hydrocarbons having a boiling point above 1000 °F (538 °C) into lower boiling hydrocarbons occurs. The effluent is then, without substantial reduction of pressure, rapidly passed through a cooling zone into a second-stage hydrocatalytic reaction zone, where hydrogenation and cracking occurs.

A major disadvantage of the process according to U.S. Patent No. 4,564,439 is the fact that the contaminated solid particles resulting from the first stage of the process are passed into the hydrocatalytic reaction zone together with the demetallised feedstock. This will usually cause a more rapid and highly unwanted decrease of the activity of the hydrocracking catalyst. Moreover, in said U.S. patent a clear preference for heavy hydrocarbonaceous feedstocks containing very high amounts of metallic contaminants is expressed. Since a deasphalting treatment generally causes a substantial amount of the metallic contaminants present in the feed as high-molecular weight complexes to accumulate in the asphaltic bitumen fraction rather than in the deasphalted oil fraction, the metals content of a deasphalted oil is usually lower than 100 ppmw.

It is therefore an object of the present invention to provide a hydroconversion process which does not have the disadvantages of the process described above. More specifically, it is an object of the present invention to provide a hydroconversion process which combines effectiveness, in terms of upgrading of residual hydrocarbon oils, process integration aspects and distillate yield, with optimum catalyst life and catalyst activity for the catalysts employed in hydrodemetallisation and hydrocracking treatments.

Accordingly, the present invention relates to a process for the conversion of a residual hydrocarbon oil, preferably a vacuum hydrocarbon oil residue, comprising the following steps:

(a) deasphalting the residual hydrocarbon oil producing an asphaltic fraction and a deasphalted oil (DAO);

(b) passing the DAO through a bed of a hydrodemetallisation catalyst in the presence of hydrogen under demetallising conditions, producing an upgraded DAO; and

(c) blending the upgraded DAO with one or more flashed distillate fractions and subjecting the resulting blend stream to hydrocracking, producing one or more distillate fractions.

The residual hydrocarbon oil feed and the flashed distillate fraction(s) used in step (c) may originate from different sources and may be supplied as separate feedstocks. It is, however, preferred that said residual hydrocarbon oil and said flashed distillate fraction(s) used in step (c) are both produced in a vacuum distillation step prior to step (a). Accordingly, in a preferred embodiment of the present invention a hydrocarbon oil, suitably

an atmospheric residue, is converted via the subsequent steps of:

(a') subjecting the residual hydrocarbon oil to vacuum distillation, producing one or more flashed distillate fractions and a residual hydrocarbon oil fraction;

(a) deasphalting the residual hydrocarbon oil fraction obtained in step (a') producing an asphaltic fraction and a deasphalted oil (DAO);

(b) passing the DAO through a bed of a hydrodemetallisation catalyst in the presence of hydrogen under demetallising conditions, producing an upgraded DAO; and

(c) blending the upgraded DAO with one or more of the flashed distillate fractions produced in step (a') and subjecting the resulting blend stream to hydrocracking, producing one or more distillate fractions.

Vacuum distillation can be carried out by any conventional technique known in the art. Suitable techniques then, include high vacuum distillation using steam ejectors and vacuum flash distillation.

The deasphalting of the heavy residual fraction obtained from the vacuum distillation may be carried out in any conventional manner. A well known and suitable deasphalting method is solvent deasphalting, wherein the hydrocarbon feed is treated counter-currently with an extracting medium which is usually a light hydrocarbon solvent containing paraffinic compounds. Commonly applied paraffinic compounds include C_{3-8} paraffinic hydrocarbons, such as propane, butane, isobutane, pentane, isopentane, hexane or mixtures of two or more of these. For the purpose of the present invention, it is preferred that C_3-C_5 paraffinic hydrocarbons, most preferably butane, pentane or a mixture thereof, are used as the extracting solvent. In general, the extraction depth increases at increasing number of carbon atoms of the extracting solvent. In this connection it is noted that the higher the extraction depth, the larger the amount of hydrocarbons being extracted from the hydrocarbon feed, the smaller and more viscous the asphaltene fraction and the heavier the asphaltenes being present in said asphaltene fraction.

In the solvent deasphalting treatment a rotating disc contactor or a plate column can be used with the hydrocarbon feed entering at the top and the extracting solvent entering at the bottom. The lighter hydrocarbons which are present in the residual hydrocarbon oil dissolve in the extracting solvent and are withdrawn at the top of the apparatus. The asphaltenes which are insoluble in the extracting solvent are withdrawn at the bottom of the apparatus. The conditions under which deasphalting takes place are known in the art. Suitably, deasphalting is carried out at a total extracting solvent to residual hydrocarbon oil ratio of 1.5 to 8 wt/wt, a pressure of from 1 to 50 bar and a temperature of from 160 to 230 °C.

Demetallisation of the DAO in accordance with step (b) of the process according to the present invention, can be achieved by any well known demetallisation process wherein the hydrocarbon feed to be demetallised is passed at elevated temperature and pressure and in the presence of hydrogen in an upward, downward or radial direction, through one or more vertically disposed reactors containing a fixed or moving bed of demetallisation catalyst particles. Well known demetallisation operations are the bunker flow operation, the fixed bed operation, the fixed bed swing operation and the movable bed operation.

As already described in the introductory part of this specification, suitable demetallisation catalyst usually consist of oxidic carriers such as alumina, silica or silica-alumina, on which one or more Group VIB or Group VIII metals or metal compounds may be deposited. Such demetallisation catalysts are commercially available from many catalyst suppliers. Particularly suitable demetallisation catalysts are those having as the active agent one of the combinations nickel/molybdenum (NiMo) or cobalt/molybdenum (CoMo), optionally promoted with phosphorus (P), on an alumina (Al_2O_3) carrier. Concrete examples of particularly suitable catalysts are $CoMo/Al_2O_3$, $CoMoP/Al_2O_3$ and $NiMo/Al_2O_3$ and $NiMoP/Al_2O_3$ catalysts. It is well known that the type of catalysts described hereinbefore in practice will also exhibit some upgrading activity in terms of hydrodenitrification and/or hydrodesulphurization, removal of heavy hydrocarbons and conversion of hydrocarbons having a boiling point above 520 °C into lower boiling components. For this reason the DAO leaving the hydrodemetallisation zone is referred to as "upgraded DAO" instead of demetallised DAO. Hydrodemetallisation is usually carried out at a hydrogen partial pressure of 20-250 bar, a temperature of 300-470 °C, preferably 310-440 °C, and a space velocity of 0.1-10 $l.l^{-1}hr^{-1}$, preferably 0.2 to 7 $l.l^{-1}hr^{-1}$.

The blending ratio of the upgraded DAO and the flashed distillate fractions is not particularly critical and is mainly determined by factors such as hydrocracking catalyst choice, viscosity specification of the hydrocracking equipment and desired product distribution in the hydrocarbon effluent. Suitably, the weight ratio flashed distillates to upgraded DAO is in the range of from 10/90 to 90/10, preferably 25/75 to 75/25 and even more preferably 40/60 to 70/30.

The hydrocracking performed in step (c) of the process according to the present invention may be conducted in any way known in the art, provided that at least one of the catalysts used in the hydrocracking zone is acidic. Generally, such process is carried out in the presence of hydrogen and a suitable hydrocracking catalyst at elevated temperature and pressure. Hydrocracking catalysts usually consist of one or more metals from

nickel, tungsten, cobalt and molybdenum in elemental, oxidic or sulphidic form on a suitable carrier such as alumina, silica, silica-alumina or a zeolite. There are many commercially available hydrocracking catalysts which can be suitably applied in the process of the present invention. At least one of the catalysts used in the hydrocracking zone must be acidic, i.e. must contain a silica-alumina and/or zeolitic component.

The hydrocracking process can be a single- or multiple-staged process. In the case of a single-staged process, a stacked bed of a hydrodenitrification/first-stage hydrocracking catalyst on top of a conversion catalyst can suitably be used. Particularly suitable hydrodenitrification/first-stage hydrocracking catalysts are $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, optionally promoted with phosphorus and/or fluor. Preferred conversion catalysts are those based on NiW/zeolite or NiW/zeolite/silica-alumina. Common hydrocracking conditions are an operating pressure of 80-250 bar, preferably 100-200 bar, and a temperature of 300-500 °C, preferably 350-475 °C.

In order to achieve optimum demetallisation of the DAO in combination with optimum distillate yield from hydrocracking it is preferred that the hydrodemetallisation of the DAO in step (b) is carried out at a hydrogen partial pressure which is at most 30 bar and suitably less than 20 bar higher than the operating pressure of the hydrocracking in step (c). Most suitably the hydrogen partial pressure in step (b) is from 0 to about 10 bar higher than the operating pressure in step (c). In this connection it is particularly preferred to apply a hydrogen partial pressure in the hydrodemetallisation zone in the range of from 150 to 200 bar. Accordingly, the operation pressure in the hydrocracking zone is suitably in the range of from 120 to about 200 bar, preferably from 140 to 180 bar.

Beside the distillate fractions there can also be produced a heavy fraction in the hydrocracking of step (c). This heavy fraction can suitably be recycled in order to be subjected to hydrocracking and/or hydrodemetallisation once again. Alternatively, said heavy fraction could also be suitably applied as a feed for a fluidised bed catalytic cracking (FCC) unit or as a feedstock for lubricating oil manufacture. Of course, a combination of these options is possible as well. In order to achieve an optimum distillate yield, it is preferred that at least a part of the heavy fraction obtained in step (c) is again subjected to hydrocracking.

The asphaltic fraction resulting from the solvent deasphalting treatment in step (a) of the process according to the present invention, may be used in several ways. It can for instance be combusted for cogeneration of power and steam. Alternatively, it can be partially combusted for clean fuel gas production, cogeneration of power and steam, hydrogen manufacture or hydrocarbon synthesis. Still another option is application in bitumen, emulsion fuels or solid fuels by means of pelletizing. A preferred option is to subject the asphaltic fraction resulting from the deasphalting treatment in step (a) to partial combustion.

Figure 1 depicts a preferred embodiment of the process according to the present invention, wherein the vacuum distillation step has been integrated.

Figure 2 depicts a further preferred embodiment of the process according to the present invention.

Figure 3 shows how the process according to the present invention can be suitably integrated in a complex hydrocracker refinery line-up.

In Figure 1 an atmospheric hydrocarbon oil residue (105) is passed into vacuum distillation zone (101), where it is separated in one or more flashed distillate fractions (106) and a vacuum residue fraction (107). At least a part of the flashed distillate fractions (106) is routed to upgraded DAO stream (110). The vacuum residue fraction (107) is deasphalted in deasphalting zone (102), resulting in an asphaltic fraction (109) and a DAO (108) which is subsequently hydrodemetallised in hydrodemetallisation zone (103). The upgraded DAO (110) is blended with at least a part of the flashed distillate fraction(s) (106) and the resulting blendstream is then passed into hydrocracking zone (104), thus producing one or more distillate fractions (111) and optionally a heavy fraction (112).

Figure 2 is in fact an extension of Figure 1 in three aspects. Firstly, in that at least a part of the heavy fraction (212) produced in hydrocracking zone (204) is recirculated by routing it to upgraded DAO (210) and blending it therewith prior to being led into hydrocracking zone (204). Secondly, part of the heavy fraction (212) routed to upgraded DAO (210) is routed to DAO (208) and blended therewith in order to be subjected to hydrodemetallisation in hydrodemetallisation zone (203) once again. This option is indicated by a dotted line in figure 2. The third aspect, finally, is also indicated with a dotted line and embodies the option of routing part of the flashed distillate fractions (206) to DAO (208) and blending it therewith. The other reference numbers used in Figure 2 correspond with those used in Figure 1 having the same last two numbers.

Figure 3 shows the line-up of a hydrocracker refinery. According to this figure a crude oil (307) is passed into atmospheric distillation zone (301), where a first separation into one or more distillate fractions (308) and a residual fraction or "long residue" (309). This long residue (309) is further separated in vacuum distillation zone (302) into one or more flashed distillate fractions (310), at least part of which is blended with upgraded DAO (317), and a vacuum residue fraction or "short residue" (311), which is deasphalted in deasphalting zone (303). Optionally, a part of the flashed distillate fractions (310) is blended with DAO (312). The DAO (312) is

passed into hydrodemetallisation zone (304) and the upgraded DAO is led into hydrocracking zone (305). The asphaltic fraction (313) resulting from the deasphalting treatment is passed into gasification zone (306) where it is partially oxidised using oxygen, supplied via stream (314), eventually producing clean fuel gas (315) and hydrogen (316). This hydrogen can for instance be passed into hydrodemetallisation zone (304) and/or hydrocracking zone (305) in order to increase the overall process efficiency. Hydrocracking in hydrocracking zone (305) results in one or more distillate fractions (318) and a heavy fraction (319), which is at least partially recirculated into hydrocracking zone (305) via blending with upgraded DAO (317). Optionally, a part of the heavy fraction (319) is blended with DAO (312).

The invention is further illustrated by the following example.

Example

A crude oil feed was subjected to conventional crude distillation; the long residue produced was subjected to conventional vacuum flashing, producing a flashed distillate (FD) and short residue (SR). The SR was subsequently subjected to solvent deasphalting using butane as extracting solvent to produce a DAO at a yield of 70% by weight based on SR.

The main properties of the SR, the DAO and the FD are listed in Table I.

The DAO and FD were coprocessed in an integrated hydro-demetallization/hydrocracking (HDM/HCU) pilot plant for about 5000 hours. The DAO was upgraded in the HDM reactor over a conventional NiMoP/alumina catalyst.

Upgraded DAO and FD were subsequently coprocessed in the HCU reactor over a catalyst system including an acidic catalyst, producing hydrowax, gasoil, kerosene, naphtha and gaseous products. Both HDM and HCU reactors were operated at the same pressure.

The operating conditions, the typical properties of the upgraded DAO, the product analysis of the final product after hydrocracking and the properties of the middle distillates produced are given in Tables II, III, IV and V, respectively.

TABLE I Properties of SR, FD and DAO

		SR	DAO	FD
Density 70/4		0.97	0.92	0.88
Viscosity, 100 °C (cSt)		1920	130	86
C	(% wt)	85.7	85.3	86.1
H	(% wt)	10.7	12.0	12.4
S	(% wt)	1.9	1.5	1.1
O	(% wt)	0.58	0.43	
N	(% wt)	0.66	0.41	0.12
Ni	(mg/kg)	41	9.2	<0.5
V	(mg/kg)	54	6.8	<0.5
Fe	(mg/kg)	154	<1.0	
Ca	(mg/kg)	34	<1.0	0.1
Na	(mg/kg)	17	<1.0	
MCR content * (% wt)		18.5	6.9	0.6
C5 asphaltenes (% wt)		19.3	0.1	
C7 asphaltenes (% wt)		7.8	<0.1	

* MCR content: content of Micro Carbon Residue, i.e. molecules which are highly aromatic

TABLE II Applied HDM and HCU process conditions

FD/DAO fresh intake rate (kg/kg)		1.16
HDM reactor		
Total Inlet pressure	(bar)	171
WHSV	(kg DAO/1.h)	0.6
Gasrate	(Nl H_2/kg DAO)	1000
HCU reactor		
Total Inlet pressure	(bar)	171
WHSV	(kg fresh FD+DAO/1.h)	0.6
Gasrate	(Nl H_2/kg fresh FD+DAO)	2000
CFR*	(kg combined feed/kg fresh FD+DAO)	1.6

* CFR: Combined Feed Ratio

TABLE III

Typical properties of upgraded DAO	
Density 70/4	0.90
Viscosity, 100 °C (cSt)	62
C (% wt)	86.7
H (% wt)	12.6
S (% wt)	0.26
N (% wt)	0.27
Ni (mg/kg)	0.5
V (mg/kg)	<0.5
MCR content (% wt)	3.0

From a comparison between Tables I and III it can be seen that Ni and V were effectively removed in the HDM process, while the MCR and N content was also significantly reduced.

TABLE IV

Product analysis after hydrocracking	
Product fraction	Yield (% wt on fresh feed)
$H_2S+NH_3+H_2O$	1.94
C_1-C_4	3.90
C_5-90 °C	4.51
90-130 °C	6.10
130-150 °C	5.28
150-180 °C	6.21
180-210 °C	6.69
210-250 °C	8.69
250-300 °C	10.81
300-500 °C	11.60
350-370 °C	5.65
>370 °C	30.81

TABLE V

Typical properties of middle distillates produced					
Product fraction	S mg/kg	N mg/kg	d(20/4)	Cetane number	Smoke point mm.
150-180 °C	<10	1	0.79		25
180-210 °C	<10	2	0.83		22
210-250 °C	<10	<1	0.83	43	21
250-300 °C	<10	1	0.85	48	
300-340 °C	<10	1	0.85	59	
340-370 °C	14	3	0.85	65	

From Table V it can be seen that high quality middle distillates were produced. The lighter middle distillate fractions (in kerosene range), useful as jet fuel, have excellent smoke points, whilst the heavier middle distillate fractions (in gas oil range), useful as e.g. diesel fuel, have very good cetane numbers. Furthermore, it can be seen that all middle distillates have very low sulphur and nitrogen contents which is very attractive from an environmental viewpoint.

Claims

1. Process for the conversion of a residual hydrocarbon oil, preferably a vacuum hydrocarbon oil residue, comprising the following steps:
   (a) deasphalting the residual hydrocarbon oil producing an asphaltic fraction and a deasphalted oil (DAO);
   (b) passing the DAO through a bed of a hydrodemetallisation catalyst in the presence of hydrogen under demetallising conditions, producing an upgraded DAO; and

(c) blending the upgraded DAO with one or more flashed distillate fractions and subjecting the resulting blend stream to hydrocracking, producing one or more distillate fractions.

2. Process according to claim 1, wherein the residual hydrocarbon oil and the flashed distillate fraction(s) used in step (c) are produced in a vacuum distillation step (a') prior to step (a).

3. Process according to claim 1 or 2, wherein the deasphalting in step (a) is carried out by a solvent deasphalting treatment, using as the extracting solvent one or more C_3-C_5 paraffinic hydrocarbons, preferably butane, pentane or a mixture thereof.

4. Process according to any one of the preceding claims, wherein step (b) is carried out at a hydrogen partial pressure which is at most 30 bar and preferably less than 20 bar higher than the operating pressure of the hydrocracking in step (c).

5. Process according to claim 4, wherein the hydrogen partial pressure in step (b) is in the range of from 150 to 200 bar.

6. Process according to any one of the preceding claims, wherein in step (c) also a heavy fraction is produced, of which at least a part is again subjected to hydrocracking.

7. Process according to any one of the preceding claims, wherein the asphaltic fraction resulting from the deasphalting treatment in step (a) is subjected to partial combustion.

8. Hydrocracker refinery wherein the process according to any one of claims 1 to 7 has been integrated.

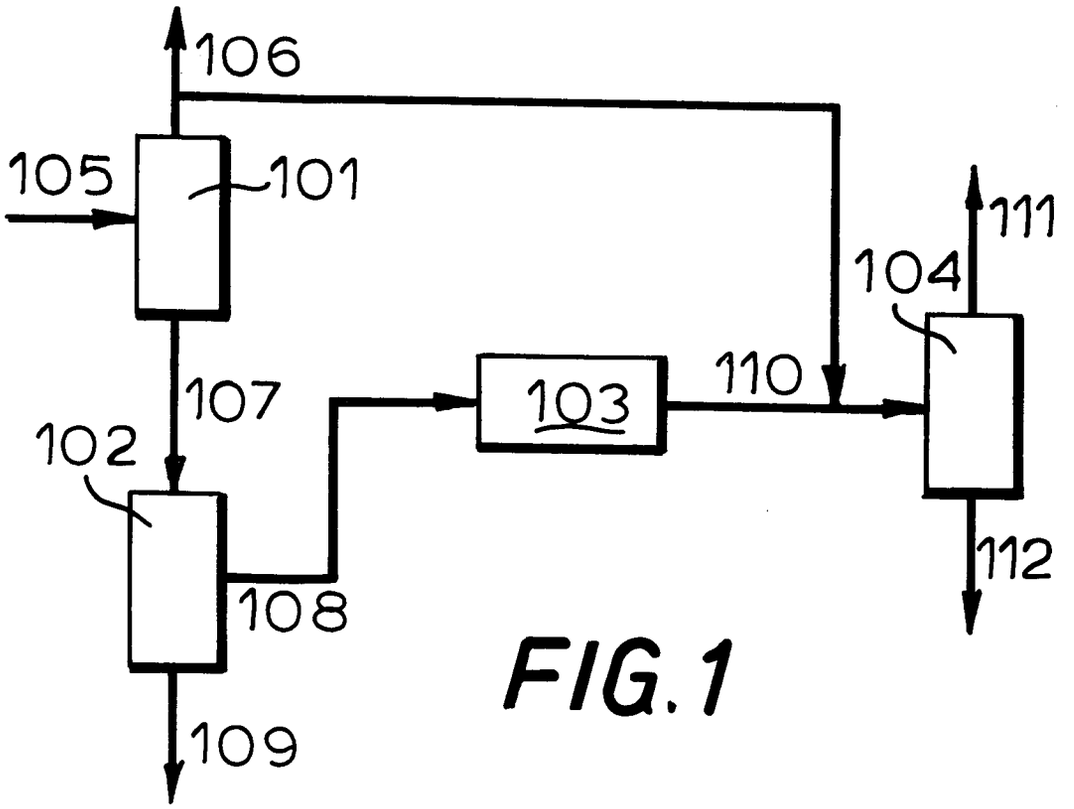
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FIG. 1

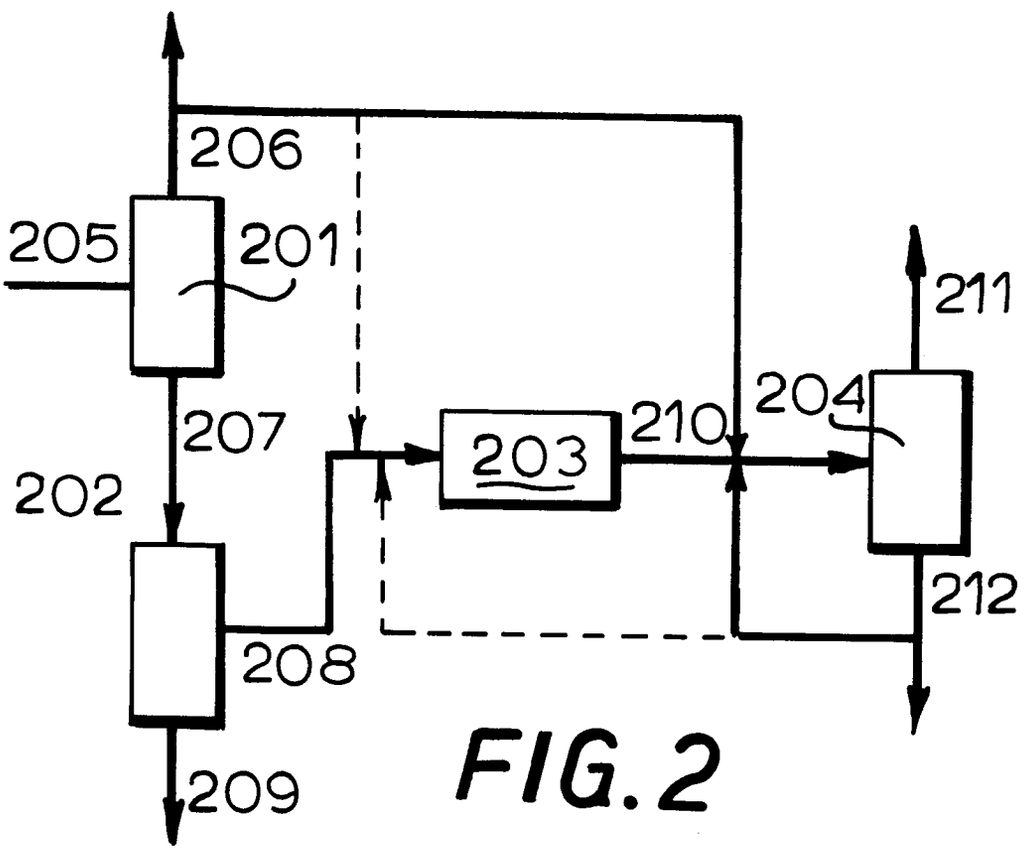
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FIG. 2

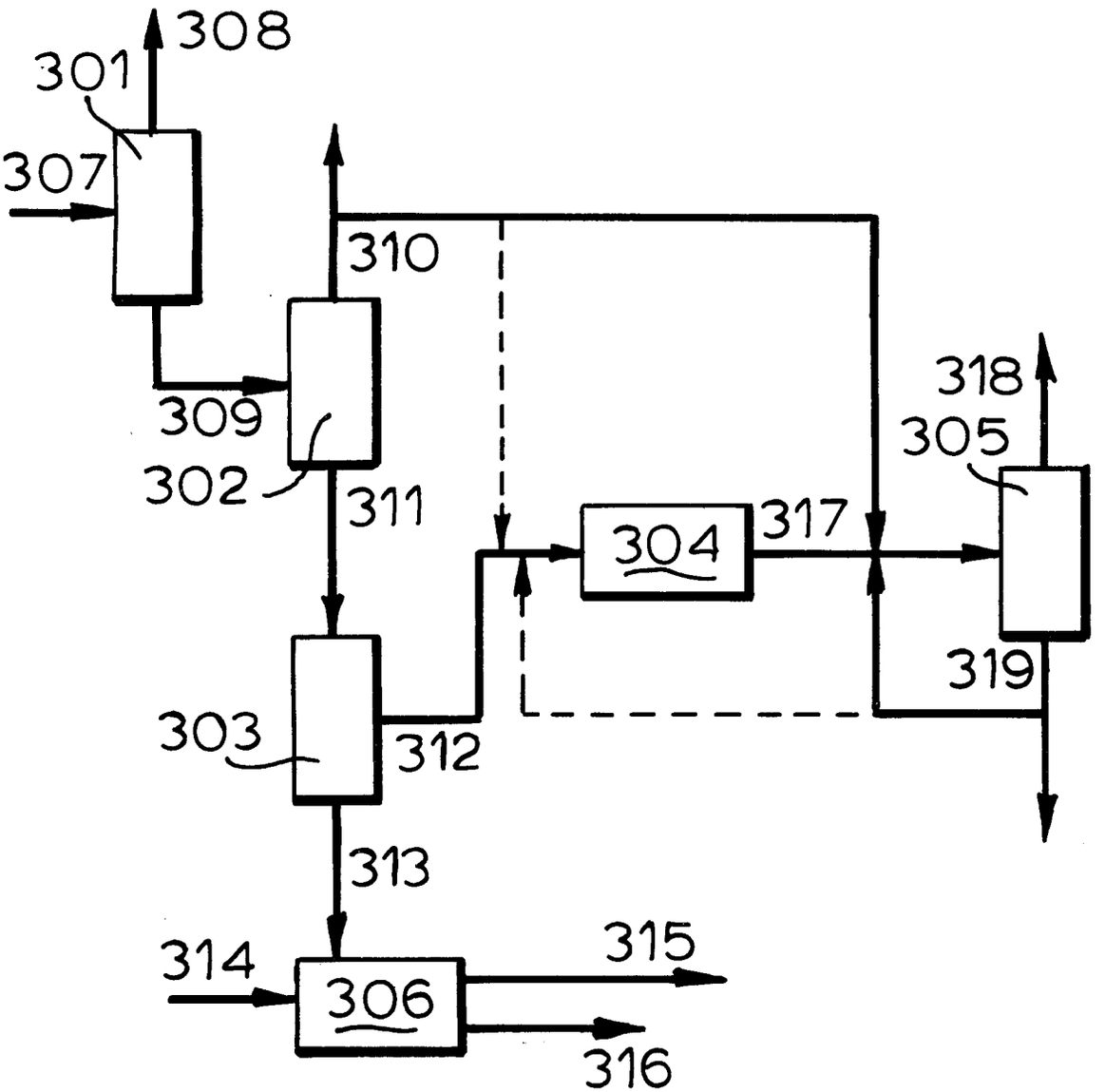
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FIG. 3