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(54) Titre : INTEGRATION DU DESASPHALTAGE AU SOLVANT A L'HYDROTRAITEMENT DE RESINE
 (54) Title: INTEGRATION OF SOLVENT DEASPHALTING WITH RESIN HYDROPROCESSING

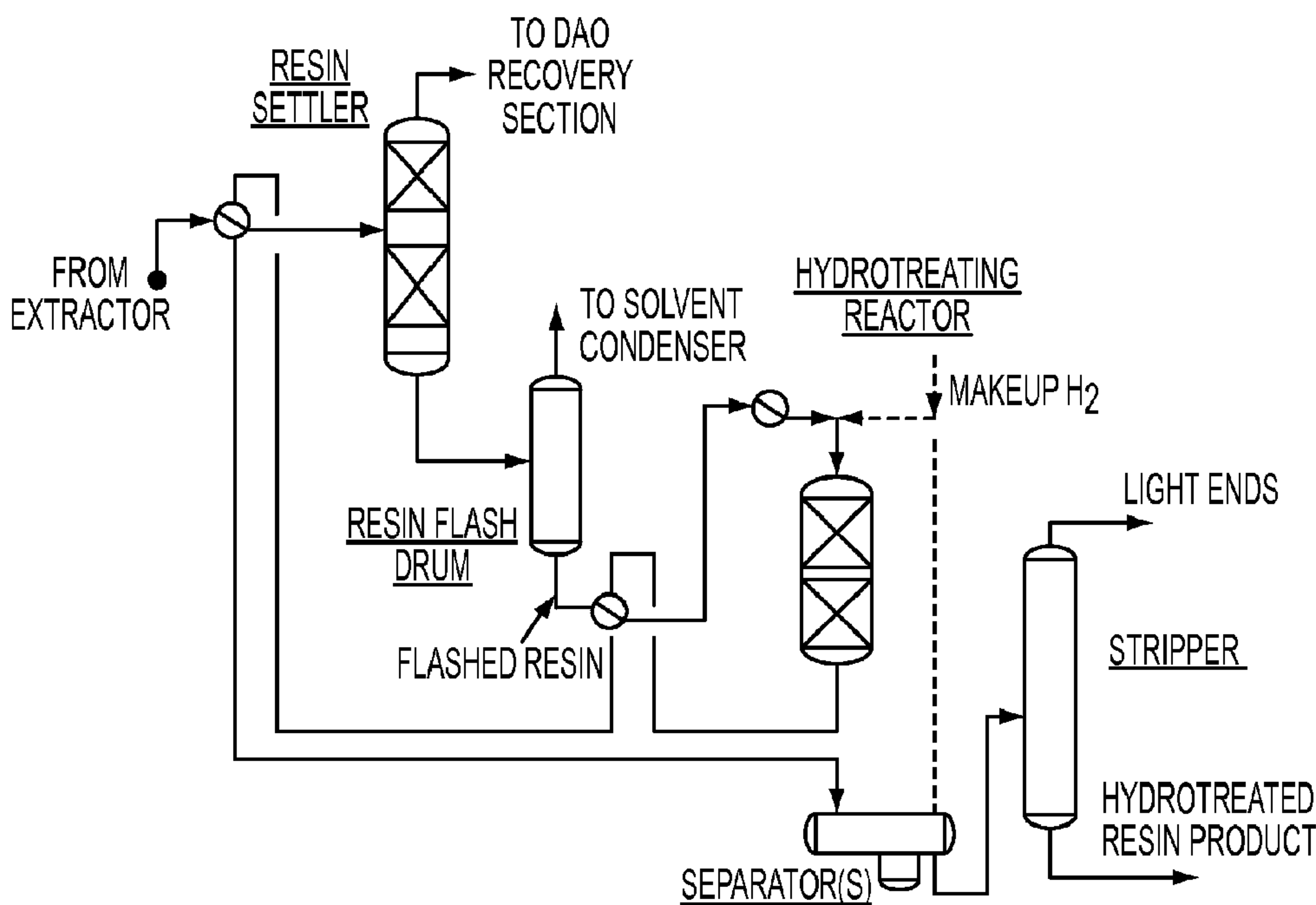


FIG. 6

(57) **Abrégé/Abstract:**

The invention is directed to a process that combines the solvent deasphalting with resin hydrotreatment so as to reduce the costs associated with performing each of the steps separately. The integrated process of the invention permits higher product yields coupled with lower energy and transportation costs.



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(54) Title: INTEGRATION OF SOLVENT DEASPHALTING WITH RESIN HYDROPROCESSING

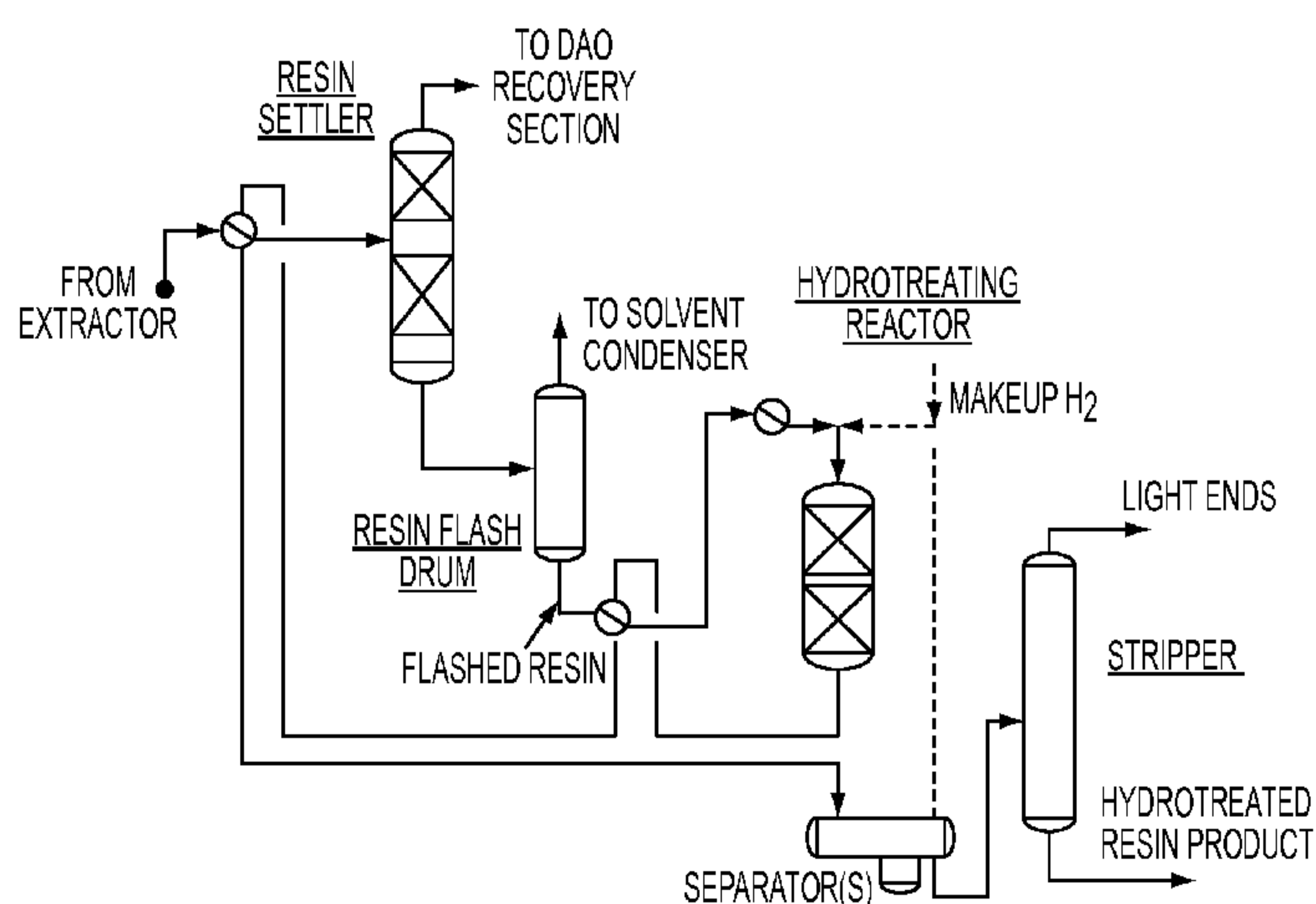


FIG. 6

(57) Abstract: The invention is directed to a process that combines the solvent deasphalting with resin hydrotreatment so as to reduce the costs associated with performing each of the steps separately. The integrated process of the invention permits higher product yields coupled with lower energy and transportation costs.

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INTEGRATION OF SOLVENT DEASPHALTING WITH RESIN HYDROPROCESSING

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This Application claims the benefit under 35 U.S.C. § 119(e) of U.S. Provisional
5 Patent Application Ser. No. 61/513,447 filed July 29, 2011, which is incorporated herein by
reference in its entirety as if fully set forth herein.

FIELD OF THE INVENTION

[0002] The invention relates to the solvent deasphalting of heavy oils coupled with resin
hydroprocessing.

10 BACKGROUND OF THE INVENTION

[0003] Conventionally, a solvent deasphalting (SDA) process is employed by an oil refinery
for the purpose of extracting valuable components from a residual oil feedstock, which is a
heavy hydrocarbon that is produced as a by-product of refining crude oil. The extracted
components are fed back to the refinery wherein they are converted into valuable lighter
15 fractions such as gasoline. Suitable residual oil feedstocks which may be used in a SDA
process include, for example, atmospheric tower bottoms, vacuum tower bottoms, crude oil,
topped crude oils, coal oil extract, shale oils, and oils recovered from tar sands.

[0004] In a typical SDA process, a light hydrocarbon solvent is added to the residual oil feed
from a refinery and is processed in what can be termed as an asphaltene separator. Common
20 solvents used comprise light paraffinic solvents. Examples of light paraffinic solvents
include, but are not limited to, propane, butane, isobutane, pentane, isopentane, neopentane,
hexane, isohexane, heptane, and similar known solvents used in deasphalting, and mixtures
thereof. Under elevated temperature and pressures, the mixture in the asphaltene separator
separates into a plurality of liquid streams, typically, a substantially asphaltene-free stream of
25 deasphalted oil (DAO), resins and solvent, and a mixture of asphaltene and solvent within
which some DAO may be dissolved.

[0005] Once the asphaltenes have been removed, the substantially asphaltene-free stream of
DAO, resins and solvent is normally subjected to a solvent recovery system. The solvent
recovery system of an SDA unit extracts a fraction of the solvent from the solvent rich DAO

by boiling off the solvent, commonly using steam or hot oil from fired heaters. The vaporized solvent is then condensed and recycled back for use in the SDA unit.

[0006] Often it becomes beneficial to separate a resin product from the DAO/resin product stream. This is normally done before the solvent is removed from the DAO. "Resins" as used
5 herein, means resins that have been separated and obtained from a SDA unit. Resins are denser or heavier than deasphalted oil, but lighter than the aforementioned asphaltenes. The resin product usually comprises more aromatic hydrocarbons with highly aliphatic substituted side chains, and can also comprise metals, such as nickel and vanadium. Generally, the resins
10 comprise the material from which asphaltenes and DAO have been removed.

[0007] Crude oils contain heteroatomic, polyaromatic molecules that include compounds
15 such as sulfur, nitrogen, nickel, vanadium and others in quantities that can adversely affect the refinery processing of crude oil fractions. Light crude oils or condensates have sulfur concentrations as low as 0.01 percent by weight (W %). In contrast, heavy crude oils and heavy petroleum fractions have sulfur concentrations as high as 5-6 W %. Similarly, the
20 nitrogen content of crude oils can be in the range of 0.001-1.0 W %. These impurities must be removed during refining to meet established environmental regulations for the final products (e.g., gasoline, diesel, fuel oil), or for the intermediate refining streams that are to be processed for further upgrading, such as isomerization or reforming. Furthermore, contaminants such as nitrogen, sulfur and heavy metals are known to deactivate or poison
25 catalysts, and thus must be removed.

[0008] Asphaltenes, which are solid in nature and comprise polynuclear aromatics present in
the solution of smaller aromatics and resin molecules, are also present in the crude oils and heavy fractions in varying quantities. Asphaltenes do not exist in all of the condensates or in
light crude oils; however, they are present in relatively large quantities in heavy crude oils
25 and petroleum fractions. Asphaltenes are insoluble components or fractions and their concentrations are defined as the amount of asphaltenes precipitated by addition of an n-paraffin solvent to the feedstock.

[0009] In a typical refinery, crude oil is first fractionated in the atmospheric distillation
column to separate sour gas including methane, ethane, propanes, butanes and hydrogen
30 sulfide, naphtha (boiling point range: 36-180°C), kerosene (boiling point range: 180-240°C), gas oil (boiling point range: 240-370°C) and atmospheric residue, which are the hydrocarbon

fractions boiling above 370°C. The atmospheric residue from the atmospheric distillation column is either used as fuel oil or sent to a vacuum distillation unit, depending upon the configuration of the refinery. Principal products from the vacuum distillation are vacuum gas oil, comprising hydrocarbons boiling in the range 370-520°C, and vacuum residue,

5 comprising hydrocarbons boiling above 520°C.

[00010] Naphtha, kerosene and gas oil streams derived from crude oils or other natural sources, such as shale oils, bitumens and tar sands, are treated to remove the contaminants, such as sulfur, that exceed the specification set for the end product(s). Hydrotreating is the most common refining technology used to remove these contaminants. Vacuum gas oil is
10 processed in a hydrocracking unit to produce gasoline and diesel, or in a fluid catalytic cracking (FCC) unit to produce mainly gasoline, light cycle oil (LCO) and heavy cycle oil (HCO) as by-products, the former being used as a blending component in either the diesel pool or in fuel oil, the latter being sent directly to the fuel oil pool.

[00011] There are several processing options for the vacuum residue fraction,
15 including hydroprocessing (including both residue hydrotreating and residue hydrocracking which includes both ebullated bed and slurry phase type reactors), coking, visbreaking, gasification and solvent deasphalting. Solvent deasphalting (SDA) is a well proven technology for separation of residues by their molecular weight and is practiced commercially worldwide. The separation in the SDA process can be into two or sometimes
20 three components, i.e., a two component SDA process or a three component SDA process. In the SDA process, the asphaltene rich fraction (pitch) comprising about 6-8 W % of hydrogen is separated from the vacuum residue by contact with a paraffinic solvent (carbon number ranging from 3-8) at elevated temperatures and pressures. The recovered deasphalted oil fraction (DAO) comprising about 9-11 W % hydrogen, is characterized as a heavy
25 hydrocarbon fraction that is free of asphaltene molecules and can be sent to other conversion units such as a hydroprocessing unit or a fluid catalytic cracking unit (FCC) for further processing.

[00012] The yield of DAO is usually set by the processing feed stock property limitations, such as organometallic metals and Conradson Carbon residue (CCR) of the
30 downstream processes. These limitations are usually below the maximum recoverable DAO within the SDA process (Table 1 and FIG. 1). Table 1 illustrates typical yields obtained in a SDA process. If the DAO yield can be increased, then the overall valuable transportation

fuel yields, based on residue feed, can be increased, and the profitability of SDA enhanced. A parallel benefit would occur with the combination of SDA followed by delayed coking. Maximizing DAO yield maximizes the catalytic conversion of residue relative to thermal conversion, which occurs in delayed coking.

5

Table 1

	<u>FEED</u>	<u>DAO</u> <u>(HC limited)</u>	<u>PITCH</u>
VOL-%	100.00	53.21	46.79
WEIGHT-%	100.00	50.00	50.00
API	5.37	14.2	-3.4
Sp.Gr.	1.0338	0.9715	1.1047
S, wt-%	4.27	3.03	5.51
N, wppm	0.3	0	0
Con Carbon, wt-%	23	7.7	38.3
C7 insols, wt-%	6.86	0.05	13.7
UOP K	11.27	11.54	11.01
Ni , ppm	24	2.0	46.0
V , ppm	94	5.2	182.8

[00013] Even without DAO downstream processing limitations, the cost of hydroprocessing DAO can be very high. In examining the DAO properties and its composition (Table 2), it can be seen that the back end of DAO, typically referred to as the Resin fraction, sets the severity and ultimately cost of the hydroprocessing unit. It would therefore be desirable to treat the Resin fraction separately in a cost-effective manner.

Table 2

	<u>FEED</u>	<u>DAO</u> <u>(HC limited)</u>	<u>RESIN</u>	<u>PITCH</u>
VOL-%	100.00	53.21	14.73	32.06
WEIGHT-%	100.00	50.00	15.00	35.00
API	5.37	14.2	2.9	-6.1
Sp.Gr.	1.0338	0.9715	1.0526	1.1287
S, wt-%	4.27	3.03	5.09	5.69
N, wppm	0.3	0	0	1
Con Carbon, wt-%	23	7.7	23.0	44.8
C7 insols, wt-%	6.86	0.02	0.1	19.5
UOP K	11.27	11.54	11.22	10.92
Ni , ppm	24	2.0	14.4	59.6
V , ppm	94	5.2	30.2	248.2

5 [00014] For applications where the only downstream hydroprocessing route is hydrocracking, the quality of the DAO is much more restrictive. Even with resin hydroprocessing, the hydroprocessed resin stream may not be suitable as VGO Hydrocracker feedstock. Therefore, further selective separation of the hydroprocessed resin stream would be beneficial to produce additional VGO Hydrocracking feedstock for those applications
10 where hydrocracking is the downstream hydroprocessing route.

SUMMARY OF THE INVENTION

[00015] An embodiment of the invention is directed to a process for deasphalting with a solvent comprising: introducing a hydrocarbon oil feedstock to an extractor; introducing a solvent to the feedstock; separating an asphaltene-containing fraction from the feedstock to
15 form an asphaltene depleted feedstock; separating a resin-containing fraction in a resin recovery section from the asphaltene separated feedstock to form a resin depleted feedstock; separating a deasphalted oil-containing fraction from the resin depleted feedstock; integrating the resin recovery section with a hydroprocessing process; and hydroprocessing the resin-containing fraction in the hydroprocessing process to generate a hydroprocessed residue
20 product.

[00016] A further embodiment of the invention is directed to a method for integrating a solvent deasphalting process and a resin hydroprocessing process comprising: adding a

solvent to a heavy hydrocarbon stream comprising asphaltenes, resin, and oil; removing the asphaltenes from the heavy hydrocarbon stream so as to produce a substantially solvent-free asphaltene stream and a substantially asphaltene-free solvent solution comprising the solvent, the resin, and the oil; heating the solvent solution so as to precipitate the resin; separating the resin from the solvent solution, producing a resin product and a mixture comprising the oil and the solvent; applying heat to the mixture so as to vaporize a fraction of the solvent; removing the vaporized solvent fraction from the mixture leaving a resin-free deasphalted oil product; hydroprocessing the resin product so as to produce a residue product; and subjecting the residue product to additional separation.

10 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the qualities of deasphalted oil relative to residue type and yield in accordance with an embodiment of the invention;

FIG. 2 shows a two product solvent deasphalting flow scheme in accordance with an embodiment of the invention;

15 FIG. 3 shows a three product solvent deasphalting flow scheme in accordance with an embodiment of the invention;

FIG. 4 shows a flow scheme for resin production in accordance with an embodiment of the invention;

20 FIG. 5 shows a hydroprocessing process flow scheme in accordance with an embodiment of the invention;

FIG. 6 shows a flow scheme for integrated resin production and hydroprocessing in accordance with an embodiment of the invention;

FIG. 7 shows a flow scheme for integrated resin production and hydroprocessing with selective separation in accordance with an embodiment of the invention; and

25 FIG. 8 shows the impact of resin hydroprocessing on coke yield in accordance with an embodiment of the invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[00017] An embodiment of the invention includes a process comprising several steps that allow an increase in DAO yield up to the limitation of the downstream hydroprocessing or FCC feedstock limitations. FIG.1 is an illustration of DAO contaminants versus DAO
5 yield for different residue types.

[00018] In an embodiment of the invention an increase in DAO yield is obtained by a process comprising the steps of separating the DAO into two fractions within the solvent deasphalting (SDA) process, namely, DAO and resins; hydroprocessing the resins in a dedicated resins hydroprocessing process; integrating the resins recovery section of the SDA
10 process with the resins hydroprocessing process, and selectively separating the hydroprocessed resin stream.

[00019] FIG. 2 is an illustration of a two-product SDA process, where the two products are DAO and pitch (asphaltenes-rich fraction).

[00020] Another embodiment of the invention shows a three-product SDA process,
15 which produces, DAO, pitch and resin. To produce the intermediate resin product, an appropriate flow scheme (FIG. 3) is required. The additional equipment includes a resin settler located between the extractor and the DAO-solvent separator, additional heat exchangers, and a resin stripper to strip entrained solvent out of the resin product (FIG. 4).

[00021] In an embodiment of the invention, hydroprocessing of residues is carried out
20 at elevated hydrogen partial pressures ranging from about 800 to about 2500 psig. In other embodiments of the invention, hydroprocessing is carried out at temperatures ranging from about 650 to about 930°F. In further embodiments of the invention, the hydroprocessing steps are performed using a catalyst made of one or more metals. Examples of metal catalysts used in embodiments of the invention include catalysts comprising iron, nickel, molybdenum,
25 and cobalt. Metal catalysts used in embodiments of the invention promote both contaminant removal and cracking of the residues to smaller molecules contained within the hydroprocessing reactor. The process conditions used in embodiments of the invention including temperature, pressure and catalyst vary depending upon the nature of the feedstock.

[00022] The hydroprocessing reactor can either be a downflow fixed-bed reactor that
30 contains catalyst in the reactor where the main objective is hydrotreating; an upflow ebullated

bed reactor where the catalyst is suspended and it may be added and withdrawn while the reactor is in operation where the objective is some conversion and hydrotreating; or an upflow slurry phase reactor where the catalyst is added to the feed and leaves with the product out of the top of the reactor where the objective is primarily conversion.

5 [00023] As used herein, the term “hydroprocessing” refers to any of several chemical engineering processes including hydrogenation, hydrocracking and hydrotreating. Each of the aforementioned hydroprocessing reactions can be carried out using the hydroprocessing reactors described above.

[00024] Additional equipment such as pumps, heat exchangers, reactor feed heater,
10 separation, and fractionation equipment may be required to support the hydroprocessing process. FIG. 5 highlights the key steps of a hydroprocessing process in accordance with an embodiment of the invention. Depending on the application, the flow scheme can be changed; however, the key steps of feed heating, reaction, and separation, and hydrogen rich gas addition and recycle are required.

15 [00025] In an embodiment of the invention, the hydroprocessing process is located downstream of the SDA process. The hydroprocessing process hydrotreats the resin fraction. The product yield benefits are fully realized with this approach.

[00026] In another embodiment of the invention the hydroprocessing process is
20 integrated with the resin section of the SDA Process (FIG. 6). This is accomplished by one or more of the following steps:

- Elimination of the resin stripper and replacement with a simpler, lower cost flash drum
- Heat integration between the reactor effluent and the feed to the resin extractor, and/or resin flash drum; and
- 25 • For low severity (low pressure) hydroprocessing applications the hydroprocessing reactor charge pump may also be eliminated.

[00027] In another embodiment of the invention the hydroprocessed resins are
30 selectively separated in an extractor (FIG. 7). In this selective separation process, the hydroprocessed resin is separated into a hydrotreated resin overhead stream and a hydrotreated resin bottoms stream. In an embodiment of the invention, the overhead stream

is sent to the DAO recovery section of the SDA section. The hydroprocessed resin bottoms stream is sent to the pitch recovery section of the SDA section.

[00028] In an embodiment of the invention, relative to delayed coking of vacuum residue, the addition of a SDA process in front of a delayed coking process reduces the coke made by 19 W %, where the DAO yield limitation is about 50 W % for a downstream VGO Hydrocracking Process. With the proposed resin draw, the coke made is reduced a further 15 W % for about a total 35 W % coke reduction compared to processing 100% vacuum residue (FIG. 8).

[00029] The above set of conditions is an example for a specific feedstock and refinery application. Specific base yields and with the proposed resin draw could have different yields.

[00030] In a further embodiment of the invention, production of more desirable products, such as transportation fuels, occurs when the resin stream is processed in a downstream catalytic conversion process. As shown in Table 3, liquid yields will typically be increased by about 5-8 W %, light hydrocarbons reduced by about 2-3 W %, and net coke made reduced by about 4 W %. It should be noted that the yields of product obtained using processes of the invention are dependent upon the nature of the feedstock material and process conditions.

Table 3

	<u>FEED</u>	<u>DAO</u> <u>(HC limited)</u>	<u>RESIN</u>	<u>RESIN</u> <u>(after Hdt)</u>	<u>PITCH</u>
VOL-%	100.00	53.21	14.73	14.16	32.06
WEIGHT-%	100.00	50.00	15.00	13.73	35.00
API	5.37	14.2	2.9	9.7	-6.1
Sp.Gr.	1.0338	0.9715	1.0526	1.0022	1.1287
S, wt-%	4.27	3.03	5.09	0.42	5.69
N, wppm	3000	1250	3000	1700	5500
Con Carbon, wt-%	23	7.7	23.0	8.5	44.8
C7 insols, wt-%	6.86	0.02	0.1	0.05	19.5
Ni, ppm	24	2.0	14.4	0.5	59.6
V, ppm	94	5.2	30.2	1.0	248.2

20

[00031] In another embodiment of the invention, selective hydroprocessing of the resin stream reduces the overall hydroprocessing costs by avoiding raising the severity of the VGO and DAO hydrocracking severity.

[00032] In certain embodiments of the invention, for applications where the downstream VGO hydrocracking process has feedstock quality limitations, the hydroprocessed resins is separated in an extractor into hydroprocessed resin DAO and hydroprocessed resin pitch streams. The selected lift in this extractor is set by the VGO hydrocracker feed quality limitations. Typically this DAO yield is over 50 W % of the hydroprocessed resin stream. Table 4 compares typical SDA yields versus the combined SDA/resin hydrotreater with selective separation yields for typical sour crude vacuum. The hydrocracking process feedstock is increased by another 12 W % of vacuum residue and the potential coke yield when the SDA Pitch is coked is decreased by another 13 W %.

Table 4

	<u>Conventional SDA</u>			<u>FW SDA-RT</u>	
	<u>FEED</u>	<u>DAO (HC limited)</u>	<u>PITCH</u>	<u>DAO+</u>	<u>PITCH</u>
VOL-%	100.00	53.2	46.8	65.4	34.9
WT-%	100.00	50.0	50.0	61.0	38.4
API	5.4	14.2	-3.4	15.2	-7.2
S, wt-%	4.3	3.0	5.5	2.6	5.2
N, wppm	3000	1250	4750	1200	5300
CCR, wt-%	23.0	7.7	38.3	7.0	42.8
C7 Ins., wt-%	6.9	0.02	13.7	0.01	17.8
Ni+V, wppm	118	7.2	229	6.0	280
Potential Coke	Base		-19%		-32%

[00033] In an embodiment of the invention, heat integration and elimination of redundant equipment between the SDA and the Resin Hydrotreater reduces the combined capital and operating costs of both processes.

[00034] The process of the invention has been described and explained with reference to the schematic process drawings. Additional variations and modifications may be apparent to those of ordinary skill in the art based on the above description and the scope of the invention is to be determined by the claims that follow.

CLAIMS

What is claimed is:

1. A process for deasphalting a solvent comprising:
 - 5 introducing a hydrocarbon oil feedstock to a reactor;
 - introducing a solvent to the feedstock;
 - separating an asphaltene-containing fraction from the feedstock to form an asphaltene depleted feedstock;
 - separating a resin-containing fraction in a resin recovery section from the asphaltene
 - 10 separated feedstock to form a resin depleted feedstock;
 - separating a deasphalted oil-containing fraction from the resin depleted feedstock;
 - integrating the resin recovery section with a hydroprocessing process; and
 - hydroprocessing the resin-containing fraction in the hydroprocessing process to generate a hydroprocessed residue product.
- 15 2. The process of claim 1, wherein the hydroprocessing process is carried out at hydrogen partial pressures ranging from about 800 to about 2500 psig.
3. The process of claim 1, wherein the hydroprocessing process is carried out at temperatures ranging from about 650 to about 930°F
4. The process of claim 1, wherein the hydroprocessing process is carried out with a catalyst.
- 20 5. The process of claim 4, wherein the catalyst is a metal catalyst.
6. The process of claim 5, wherein the metal catalyst comprises one or more metals selected from the group consisting of iron, nickel, molybdenum and cobalt.
7. The process of claim 1, wherein the hydroprocessed residue product is subjected to a further separation process.

8. The process of claim 7 wherein the further separation process comprises generating a resin overhead stream and a resin bottoms stream.
9. The process of claim 1 wherein the solvent comprises a light paraffinic solvent.
10. The process of claim 9, wherein the light paraffinic solvent is propane, butane, isobutane,
5 pentane, isopentane, neopentane, hexane, isohexane, heptane and mixtures thereof.
11. A method for integrating a solvent deasphalting process and a resin hydroprocessing process comprising:
- adding a solvent to a heavy hydrocarbon stream comprising asphaltenes, resin, and oil;
 - removing the asphaltenes from the heavy hydrocarbon stream so as to produce a
10 substantially solvent-free asphaltene stream and a substantially asphaltene-free solvent solution comprising the solvent, the resin, and the oil;
 - heating the solvent solution so as to precipitate the resin;
 - separating the resin from the solvent solution, producing a resin product and a mixture comprising the oil and the solvent;
 - 15 applying heat to the mixture so as to vaporize a fraction of the solvent;
 - removing the vaporized solvent fraction from the mixture leaving a resin-free deasphalted oil product;
 - hydroprocessing the resin product so as to produce a residue product; and
 - subjecting the residue product to additional separation.
- 20
12. The method of claim 11 wherein at least a fraction of the solvent is removed with the resin product.
13. The method of claim 12 wherein the resin product comprises about 50% resin and about
25 50% solvent.
14. The method of claim 11 wherein the resin-free deasphalted oil product is further

processed in a product cracking unit selected from the group consisting of a hydrotreater unit, a hydrocracker unit and a fluidized catalytic cracking unit.

15. The method of claim 11 wherein the resin-free deasphalted oil product comprises about
5 50% deasphalted oil and about 50% solvent.
16. The method of claim 11 wherein the solvent solution comprises about 10% deasphalted oil and resin, and about 90% solvent.
- 10 17. The method of claim 11 wherein the vaporized solvent is condensed, combined with the solvent, and added to the heavy hydrocarbon stream comprising asphaltenes, resin, and oil.
18. The method of claim 11 where the residue product is subjected to a further separation step in the SDA unit.
19. The method of claim 18 wherein the further separation step comprises generating a
15 hydrotreated resin overhead stream and a hydrotreated resin bottoms stream.
20. The method of claim 11, wherein the solvent comprises a light paraffinic solvent.
21. The method of claim 20, wherein the light paraffinic solvent is propane, butane, isobutane, pentane, isopentane, neopentane, hexane, isohexane, heptane and mixtures thereof.

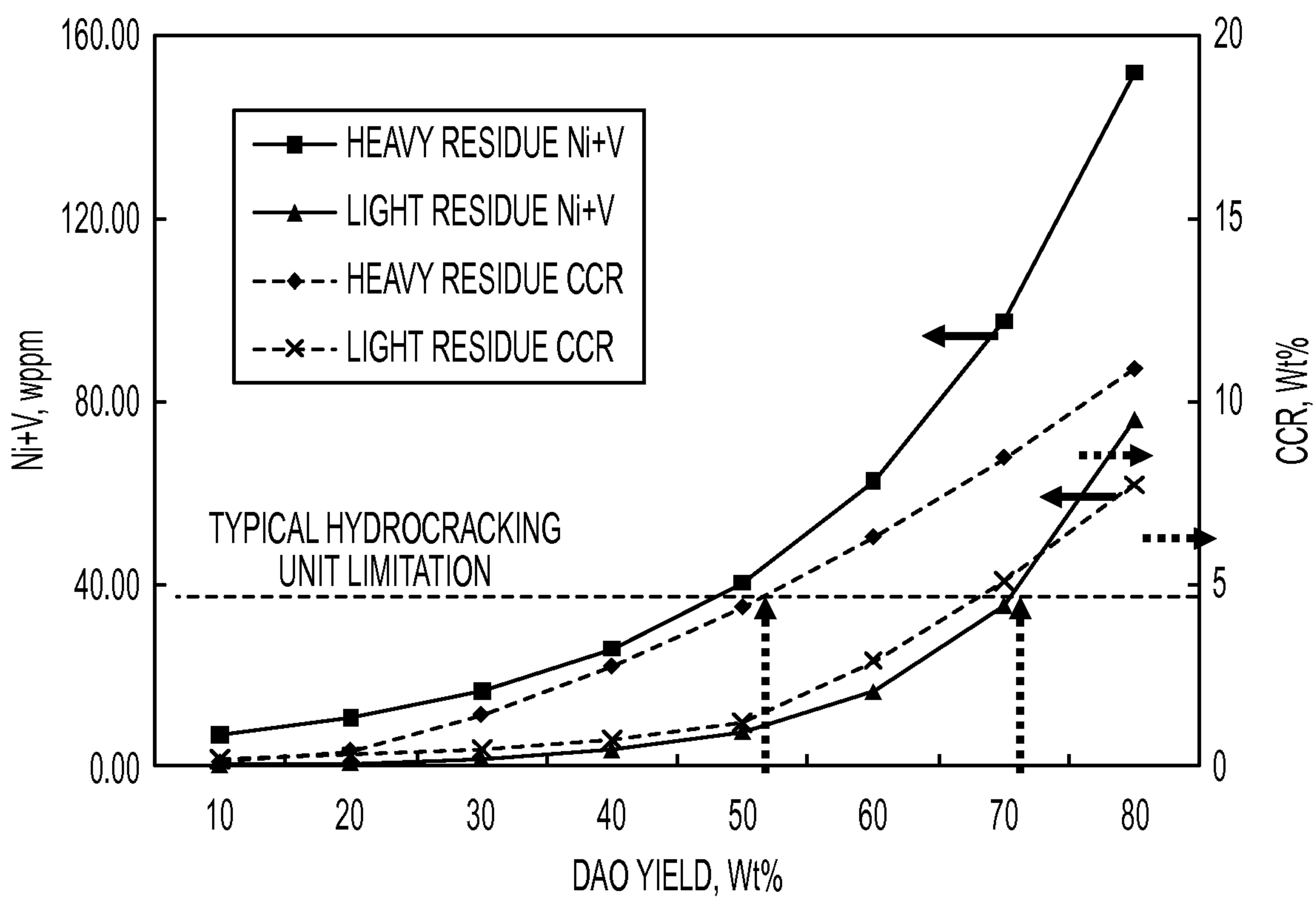


FIG. 1

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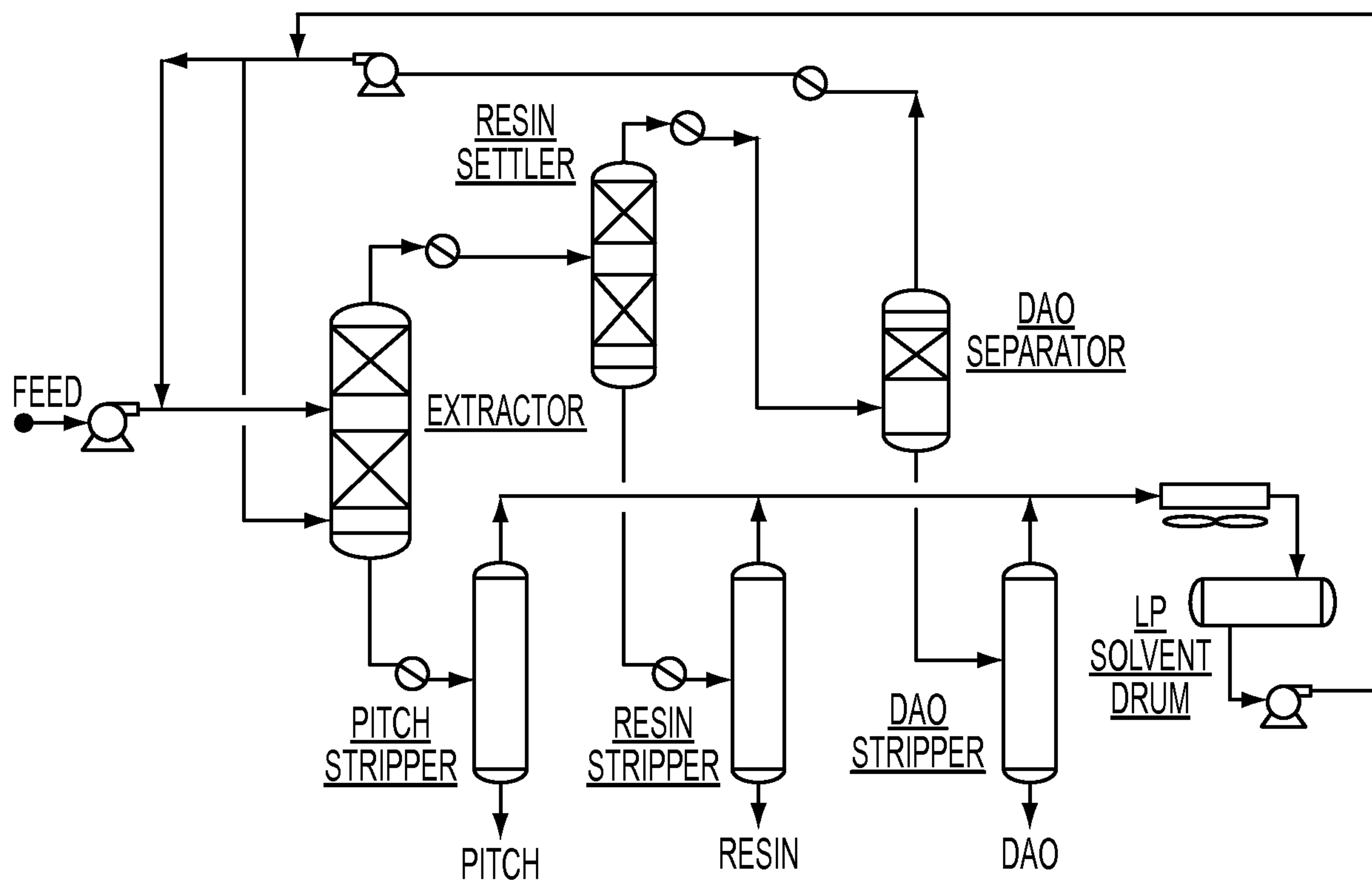


FIG. 3

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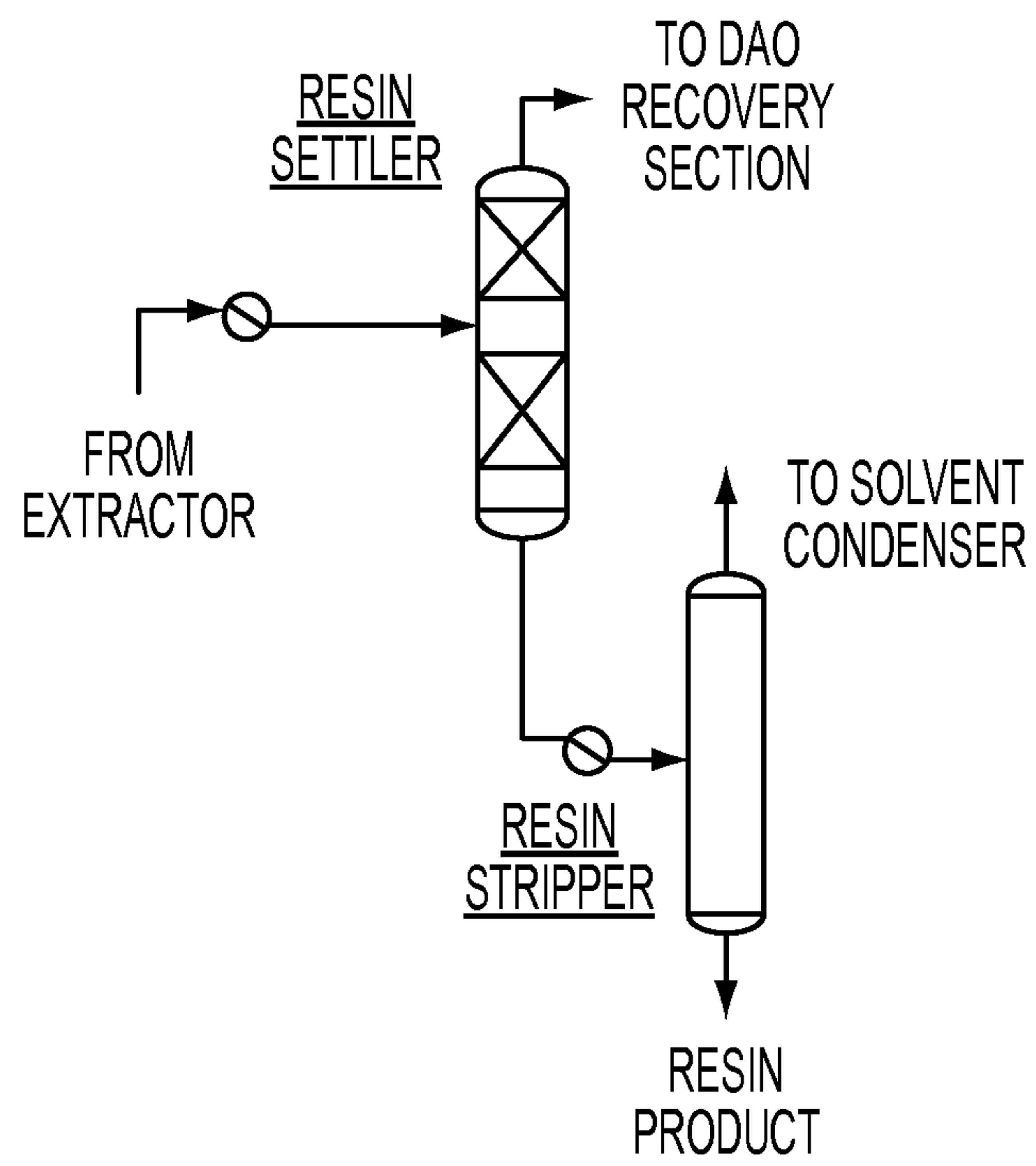


FIG. 4

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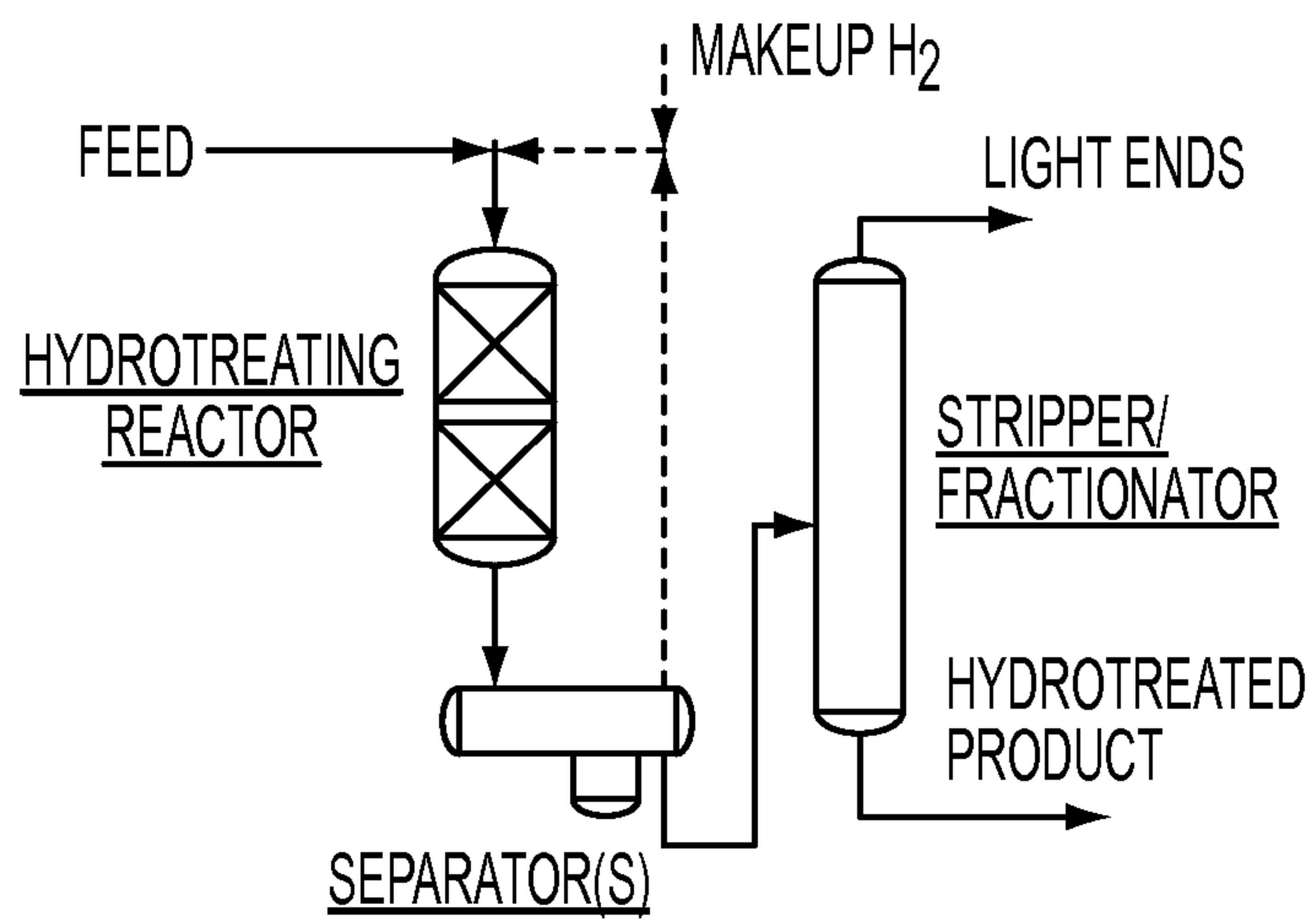


FIG. 5

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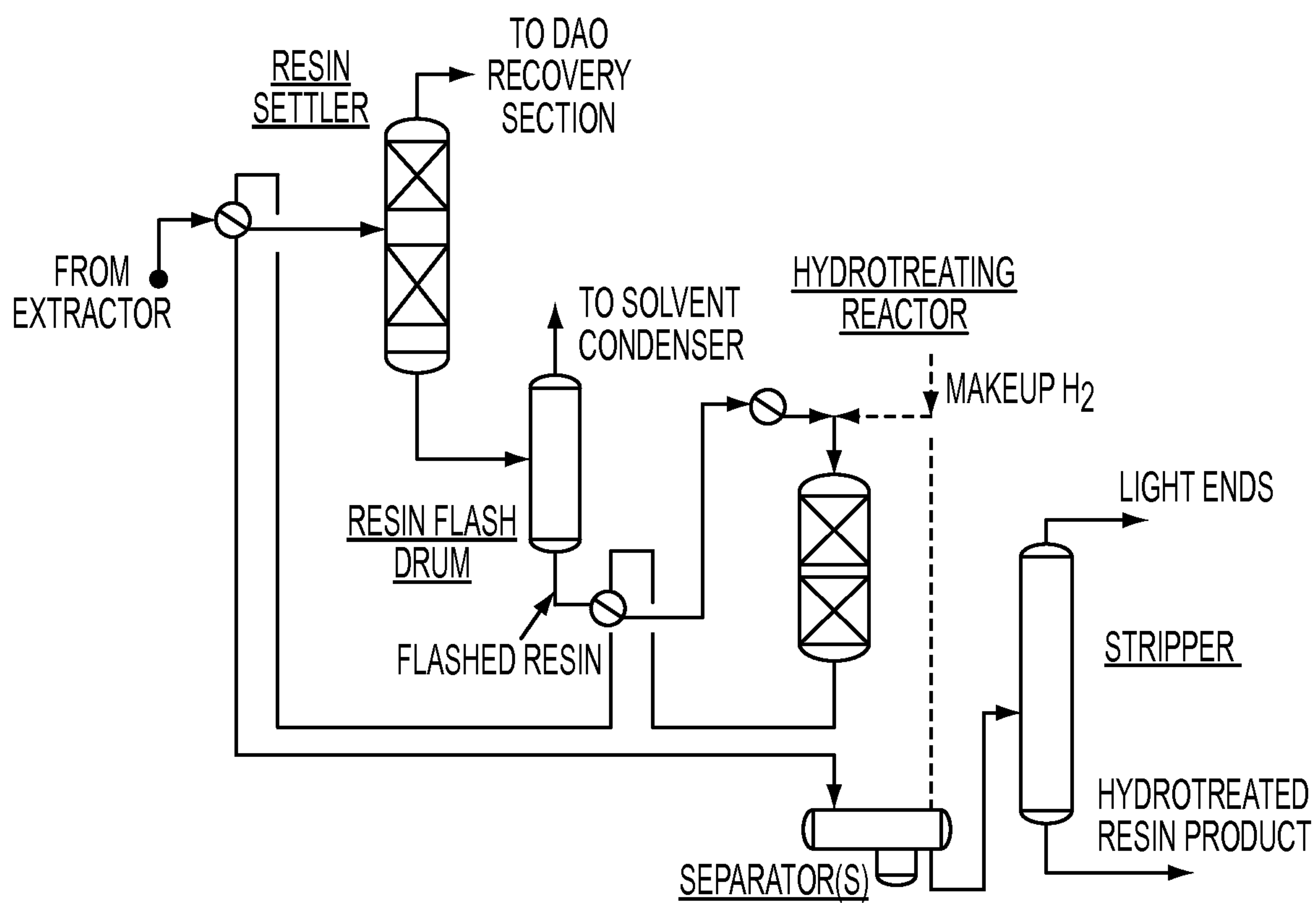


FIG. 6

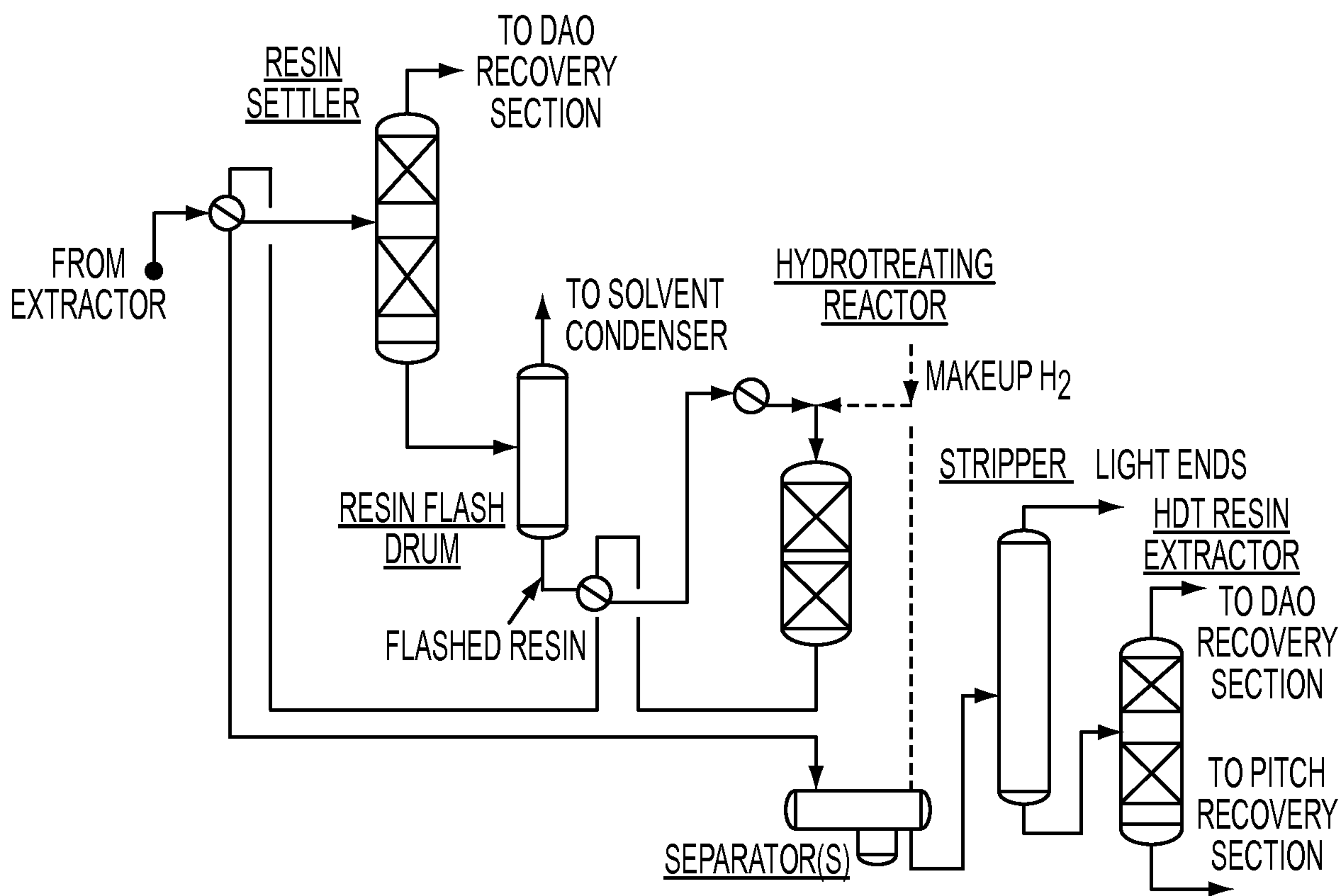


FIG. 7

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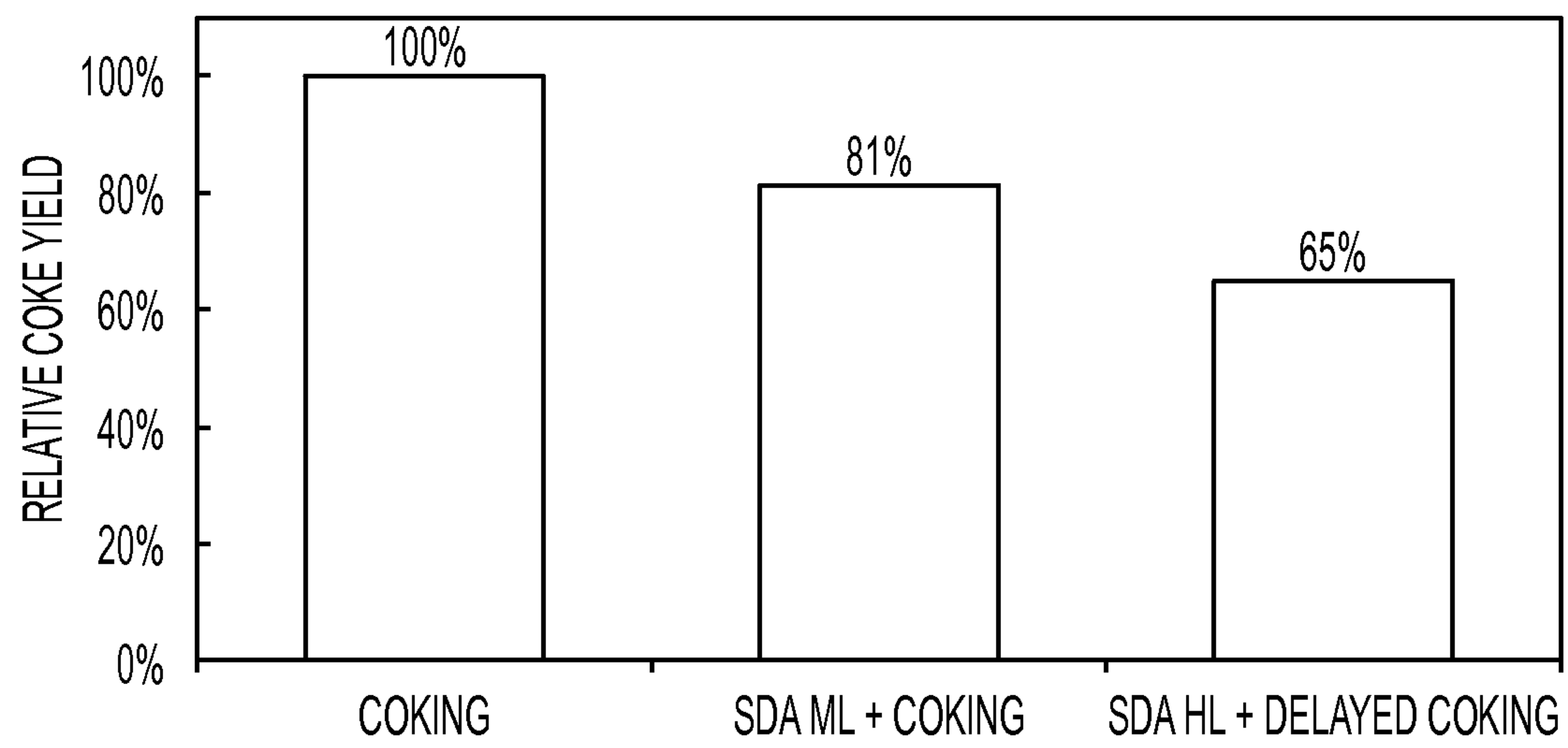


FIG. 8

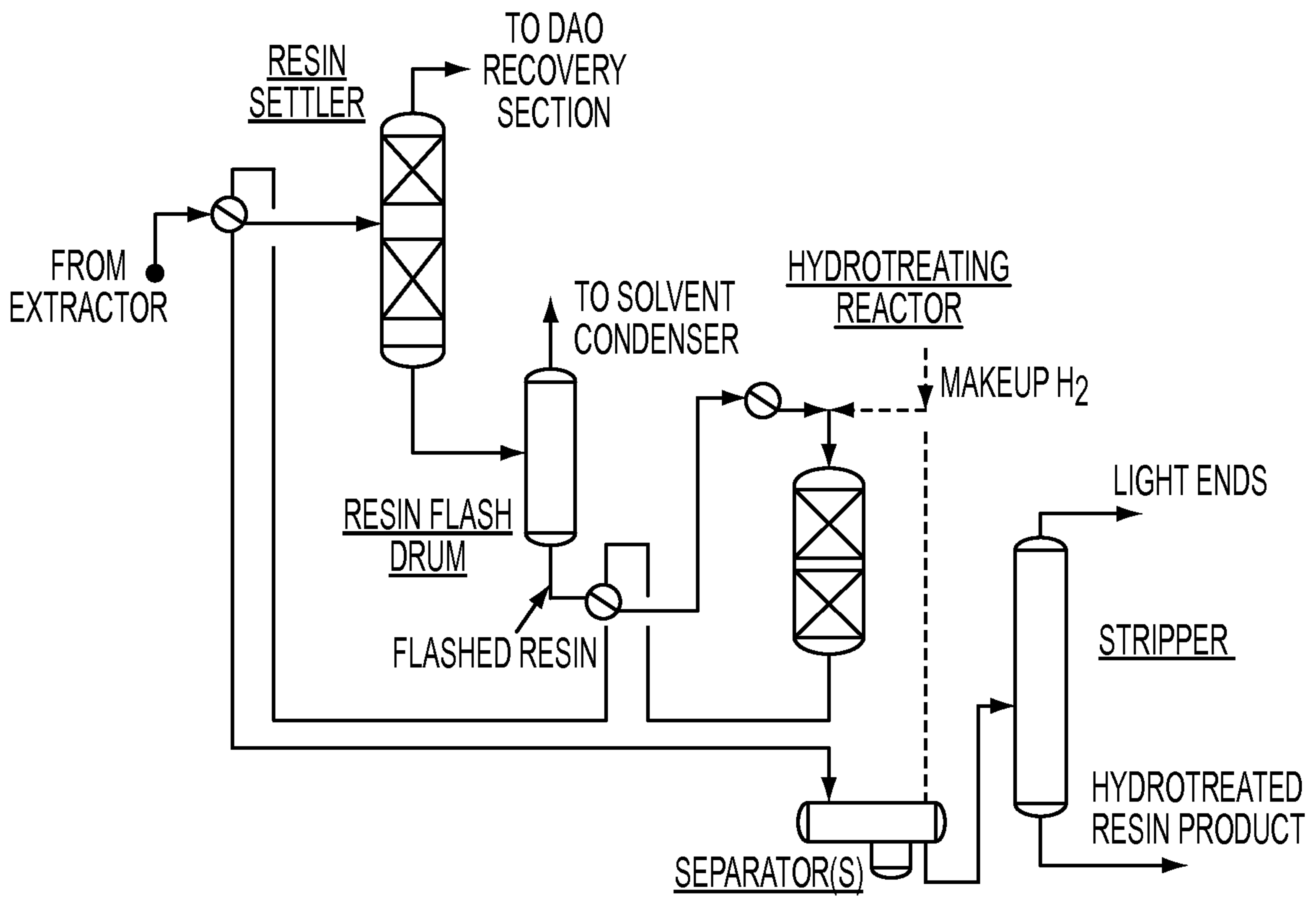


FIG. 6