Oct. 4, 1966 H. F. POLL 3,277,199

SELECTIVE HYDROFINING

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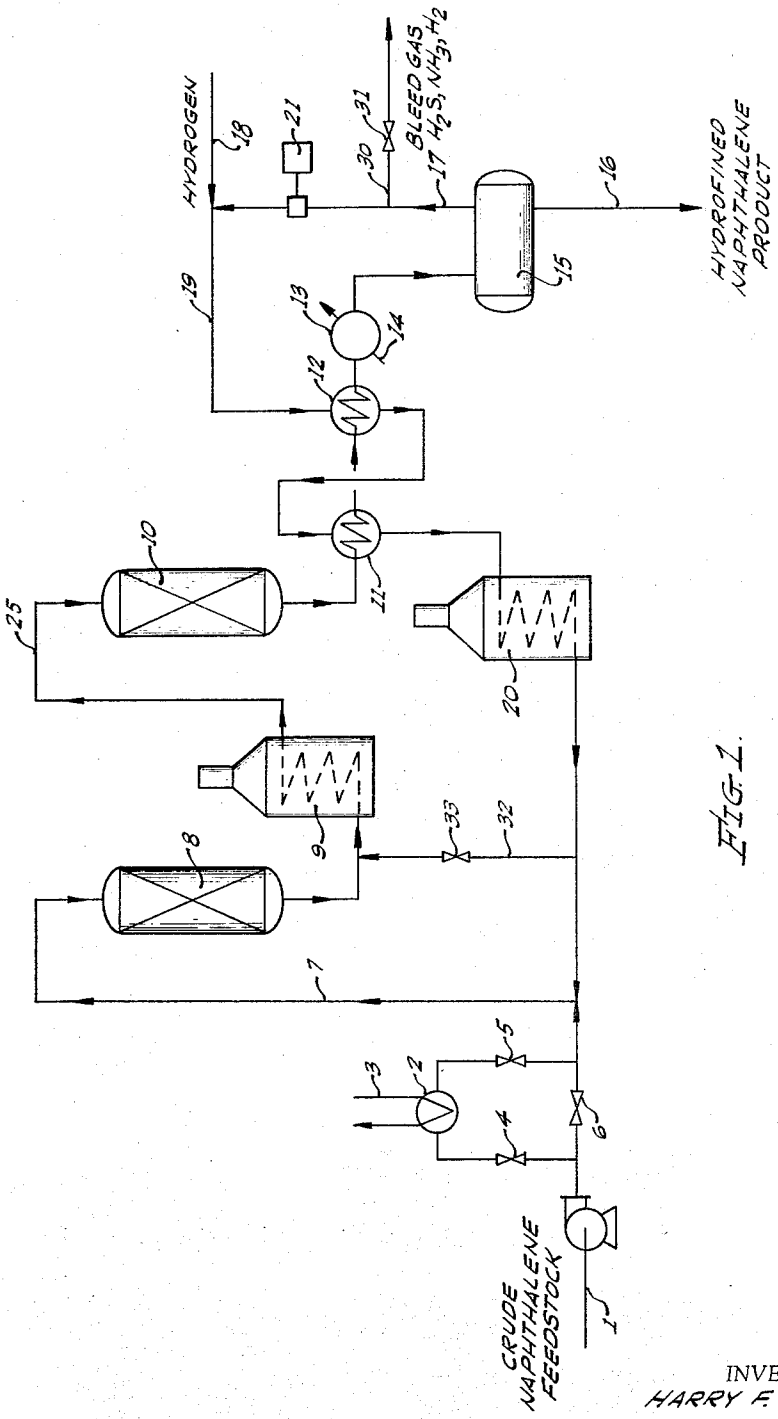

FIG. 1.

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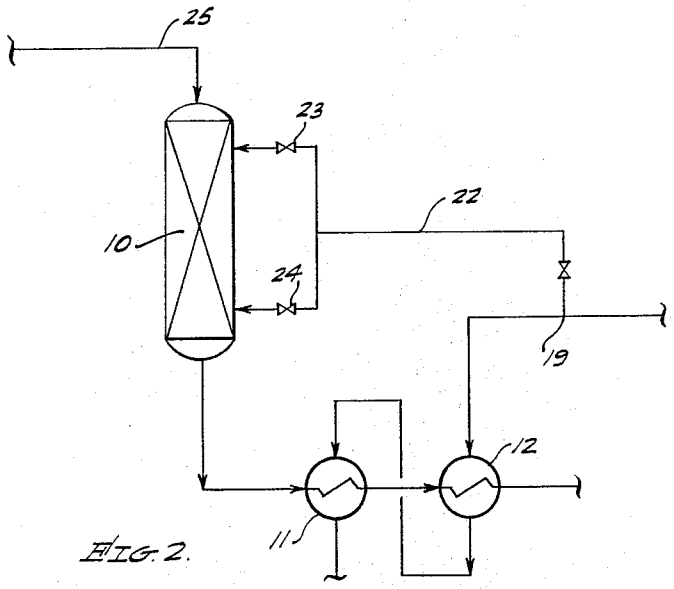

FIG. 2.

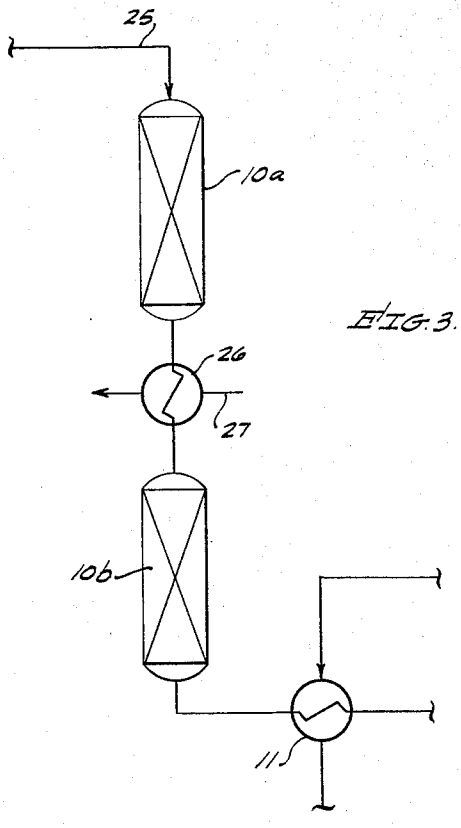

FIG. 3.

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3,277,199

Patented Oct. 4, 1966

3,277,199

SELECTIVE HYDROFINING

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Filed Jan. 22, 1962, Ser. No. 167,689
7 Claims. (Cl. 260—674)

This invention relates to a selective hydrofining process and, in particular, relates to the selective hydrofining of hydrocarbons rich in naphthalenes and associated impurities such as sulfur, nitrogen and indenes.

This invention comprises a method for the selective hydrofining of hydrocarbons rich in naphthalenes to effect a substantial reduction in the various impurities such as sulfur, nitrogen and indenes with minimum saturation of the naphthalenes to Tetralins.

Normally, it would not be expected that hydrofining of a hydrocarbon containing naphthalene could be conducted without the concurrent hydrogenation of the naphthalene nucleus. Thus, the art shows that there is more than 50 percent saturation of naphthalene at equilibrium under typical desulfurization conditions; see Journal of Physical Chemistry, 62, 1059 (1958).

I have now discovered that the hydrofining of such hydrocarbons can be kinetics controlled to permit a high degree of desulfurization and nitrogen removal before any substantial degree of naphthalene saturation occurs. I have also found that indenes can be saturated at very low temperatures where the rate of naphthalene saturation is negligible. I have also found that an increase in temperature generally accelerates the naphthalene saturation reaction to a greater extent than the desulfurization reaction.

Conventional hydrofining is normally performed in a single stage under more or less abiatic conditions. When such practice is applied to the hydrofining of naphthalene wherein exothermic reactions are encountered, e.g., hydrodesulfurization and indene hydrogenation, a temperature rise in the reactor is encountered. This conventional practice is not satisfactory for the hydrofining of naphthalene streams for the reasons described in the following paragraphs.

To achieve satisfactory desulfurization, it is necessary to have a reactant inlet temperature sufficiently high to initiate the desulfurization reaction at a favorable rate. Once initiated, however, the exothermic heat release of the reaction increases the reactant temperature to a peak temperature which is often far in excess of the desired average temperature for the desulfurization reaction. Because the increase in temperature accelerates the naphthalene saturation reaction to a greater degree than the desulfurization reaction, the optimum balance of hydrofining reactions is upset in favor of Tetralin production. This state of the art has generally precluded the use of hydrofining for naphthalene purification.

I have now found, however, that hydrocarbon streams rich in naphthalenes can be hydrofined by a method which minimizes the temperature rise normally encountered in the reaction. This temperature rise is minimized in acacordance with my invention by conducting the hydrogenation of the indene impurities associated with the naphthalene stream in a first or preliminary hydrogenation step at low temperatures and high space velocities which preclude any substantial hydrogenation of the naphthalene nucleus. If desired, some of the desulfurization can be conducted in this stage. Because the exothermic heat release from these reactions, particularly the hydrogenation of indenes, is removed from the desulfurization reactor, such heat release is not available to contribute to the temperature rise. Accordingly, the peak temperature encountered in the desulfurization reactor is minimized by the removal of this reaction.

In its preferred embodiment, the first preliminary hydrogenation of the feed is performed under liquid phase conditions and the exothermic heat release is thereby utilized to heat the charged stock to vaporization temperatures needed for the hydrodesulfurization step. The preliminary hydrogenation of the feed also saturates the diolefins and various resin and coke forming constituents in the feed which would normally cause coking in the usually employed preheat exchangers and preheater tubes of the hydrodesulfurization facilities. This greatly reduces the maintenance of the unit and increases the duration of run periods.

The hydrodesulfurization is performed in the second stage in vapor phase. If desired, the temperature rise is further minimized in this step by cooling of the reactants intermediate their conversion and/or by quenching the hydrodesulfurization reactor intermediate its bed depth.

The process will now be described in detail in reference to FIGURE 1. A hydrocarbon feedstock rich in naphthalene enters the process at line **1**. This feed is rich in naphthalenes which are derived from a variety of sources including the various mineral oil or petroleum virgin, thermally or catalytically cracked distillate stocks and the naphthalene-rich streams derived from the distillation of coal. Generally, such feed-stocks contain naphthalene, methylnaphthalenes, dimethylnaphthalenes, and various mono- and polyalkylnaphthalenes having alkyl groups with about 1 to about 10 carbon atoms. Also present are indanes, alkylbenzenes, Tetralins, etc. Such hydrocarbon stocks can be the various heavy naphthas and light cycle oils obtained by distillation of crude petroleum or, more commonly, the distillates from thermally and/or catalytically cracked an reformed hydrocarbon stocks, e.g., the light cycle oil from platforming. It is of course apparent that naphthalene rich distillates containing similar impurities can also be found in distillate products from coal distillation. The amount of naphthalene base compounds in the feedstock can vary widely depending on the nature of the feedstock and its prior treatment. Generally, however, feedstocks containing between 10 and about 95 percent naphthalene base compounds, more commonly, between about 35 and about 80 percent naphthalene and alkyl naphthalenes, are common in the aforedescribed distillates.

The aforedescribed hydrocarbon feedstocks also contain a variety of impurities which can be removed by hydrofining. Among such are: oxygen, diolefins, olefins, indenes, nitrogen, sulfur, etc. In general, nitrogen impurities are present in all the aforedescribed stock in trace amounts to several hundred parts per million and sulfur impurities are present in trace amounts to several thousand parts per million. Indenes are most prevalent in thermally cracked or converted hydrocarbon stocks and can comprise up to 30 weight percent of such stocks. Catalytically converted stocks also contain some indenes. In general, the greatest improvement attained by my invention is on hydrocarbon stocks containing between about 1 and about 30 weight percent, preferably between about 5 and about 20 weight percent, indenes.

As previously mentioned, the first stage of the hydrofining process is conducted under conditions conducive to the saturation of indenes, diolefins, and other resin and coke forming constituents of the charge stock. Preferably, a minor degree of desulfurization is also achieved in this stage; between about 1 and about 45 percent, preferably 1 to about 30 percent of the sulfur removal being effected in the first stage. In general, the temperature employed for the first stage can be between about 300° and about 550° F., preferably between about 350° and about 475° F. The naphthalene-rich fraction is normally available at a satisfactory temperature by taking it directly from the distillation facilities which produced it, without

need for any further preheat. However, when starting up from tankage supply, or under other such abnormal conditions, a sufficient preheating of the charge stock is provided by circulating all or a portion of the feed through heat exchanger **2**. A heating fluid, e.g., steam or the hot naphthalene stream from the process, can be circulated through line **3** to supply heat to the charge stock. The amount of heat input in exchanger **2** is balanced with the heat supply to the recycle gas in furnace **20** and product coolers **11** and **12** so as to achieve the desired temperature of the combined charge to reactor **8** in a manner apparent to those skilled in the art.

Liquid phase conditions are preferred in reactor **8** and, accordingly, sufficient pressure is employed to maintain the reactants in liquid phase. Generally, hydrogen partial pressures between about 10 and about 1000 p.s.i.g., preferably between about 100 and 500 p.s.i.g., can be employed. In general, a source of high purity hydrogen is available so that the partial pressure of hydrogen will comprise between about 50 and about 90 percent of the total pressure. The liquid or hourly space velocity can be varied as desired to effect the necessary severity of hydrogenation, i.e., to saturate the indene impurities. Generally, however, space velocities between about 1 and about 10 volumes per volume per hour are employed, preferably space velocities between about 3 and about 6 volumes per volume per hour. The hydrogen rich gas rate can vary between about 500 and about 10,000 standard cubic feet per barrel of feedstock; between about 2,000 and 7,000 being preferred.

In the first and subsequent stages of conversion, conventional hydrofining catalysts are used including, in general, any of the Group VIB and/or Group VIII metals, their oxides or sulfides, either as such or preferably distributed upon an adsorbent oxide carrier such as alumina, titania, zirconia, silica; alumina silicates, such as clays, zeolites, crystalline metallo alumino silicates such as molecular sieves types X, Y, Z, etc. Particularly suitable catalysts for the first stage are the various sulfur resistant catalysts which comprise a combination of an iron group metal, oxide or sulfide, with a Group VIB metal oxide or sulfide, supported upon activated alumina, or activated alumina stabilized by the addition of a small proportion (3–15%) of silica gel.

The total hydrogenating components of the catalyst can comprise between about 4 and about 25 percent by weight of the finished catalyst. Preferred catalysts are the cobalt molybdate type, which contain between about 1 and about 5 percent cobalt oxide or sulfide and between 5 and about 20 percent molybdenum oxide or sulfide. Preferably, the catalyst is subject to a presulfiding technique in order to convert the active hydrogenating components substantially completely to the sulfide form. The catalyst is preferably employed in subdivided form, e.g., pellets between about 1/16 and 1/4 inch or as 8 to about 20 mesh granules.

It is noted that the figure shows concurrent down flow of reactants and recycle hydrogen rich gas through the reactors in both the first and second stages. It is of course apparent that this is only an illustrative embodiment of the process. Other flow techniques, e.g., concurrent up flow, countercurrent flow, etc., can be substituted for the illustrated concurrent down flow as equivalent thereto in a manner apparent to those skilled in the art.

The saturation of indenes and diolefins in the first stage reactor **8** together with a minor degree of hydrodesulfurization results in an exothermic heat release which causes a temperature rise through the bed. The reactants exiting bed **8** thus have an elevated temperature of between about 310° to about 575° F., depending on their inlet temperature and, of course, the amount of indene saturation occurring in the reactor.

The average temperature in the second stage reactor **10** is generally between about 500° and about 775° F., preferably between about 550° and 700° F. This average

temperature is achieved by admitting the reactants through line **25** together with the hydrogen rich gas as illustrated, preheated to a temperature between about 475° and 750° F., preferably between about 525° and about 650° F. In many instances, the exothermic heat release in the first stage reactor **8** may be insufficient to preheat the reactants to the necessary inlet temperature for reactor **10**. On such occasions, it is within the scope of the invention to employ preheater **9**.

The hydrogen partial pressure maintained in reactor **10** can be varied as desired to effect the necessary degree of hydrodesulfurization. In general, hydrogen partial pressures between about 10 and 1000 pounds per square inch, preferably between about 100 and 500 p.s.i.g., are employed, and this partial pressure is generally 50 to about 90 percent of the total pressure in the second stage. The liquid hourly space velocities likewise can be varied to effect the necessary hydrodesulfurization of the charge stock. In general, low space velocities tend to shift the reaction in favor of Tetralin production. Accordingly, relatively high space velocities are employed, generally in amounts between about 1 and about 10 volumes per volume per hour, preferably between about 1 and about 5 volumes per volume per hour. The hydrogen gas rate can be the same as in the first stage or can be widely varied, between about 500 and about 10,000 standard cubic feet per barrel; preferably between about 4000 and about 8000. As previously mentioned, the catalyst for the second stage can be any of the aforementioned conventional hydrofining catalysts, preferably the cobalt molybdate type.

The effluent from the hydrodesulfurization reactor **10** is passed through the tube bundles of heat exchangers **11** and **12** in indirect heat exchange with the recycle hydrogen rich gas and finally through water cooler **13**. The cooled products are passed to gas separator **15** and the hydrofined naphthalene and alkylnaphthalene product is withdrawn through line **16** to suitable hydrogen sulfide stripping facilities. The alkylnaphthalenes so recovered can then be thermally or catalytically dealkylated to yield a product rich in naphthalene.

The recycle gas is withdrawn from separator **15** through line **17**, compressed by compressor **21** and recycled to the process through line **19**, the shell side of exchangers **11** and **12** and, finally, through furnace **20** when additional heat is needed for the reactant feed to the reactor **8**. The preheated hydrogen rich gas stream is commingled with the crude feedstock in line **7**. If countercurrent contacting is desired in reactor **8**, it is of course apparent that such hydrogen rich gas stream would be separately supplied to this reactor rather than commingled with the crude feedstock.

As previously mentioned, it is within the scope of my invention to employ cooling means in the hydrodesulfurization reactor **10** so as to further minimize the peak temperature encountered therein. Such an embodiment is illustrated in the FIGURE 2 wherein line **22** and valves **23** and **24** are added to the facilities illustrated in FIGURE 1. The facility thus illustrated comprises a quench supply of cool recycle gas from recycle line **19**. This gas can be admitted in any desired amount by control of valves **23** and **24** so as to maintain the desired temperature profile within the reactor.

Other techniques for cooling the reactants intermediate their conversion in reactor **10** will of course be apparent to those skilled in the art. Such techniques can comprise, for instance, the use of a cooling coil throughout the entire depth of the catalytic bed in reactor **10**, or at any level therein, together with means to supply a cool heat exchange fluid therethrough. Other facilities such as illustrated in FIGURE 3 could comprise the division of the bed **10** into two or more reactors **10*a*** and **10*b*** with an intermediate cooler **26** having a heat exchange supply **27**. In any event, sufficient cooling can be achieved by quenching or indirect heat exchange so as to maintain

the temperature fairly constant in reactor **10**, i.e., to maintain isothermal conditions.

The following examples will illustrate the invention:

EXAMPLE 1

A 1-inch schedule 80 stainless steel pipe was employed as a reactor and filled with 220 ml. of a cobalt molybdate catalyst. A hydrogen rich gas stream was commingled with the naphthalene rich charge stock and the resultant stream was preheated to the desired inlet temperature and admitted to the top of the reactor for a downward concurrent flow therethrough. The naphthalene charge stock had the following properties:

Naphthalenes/alkylnaphthalenes	percent	73.7
Indenes	do	12.1
Sulfur	p.p.m.	700
Gravity	° API	9.3

Prior to introduction of the naphthalene charge stock, the cobalt molybdate catalyst was presulfided by flowing through a 4% thiophene solution in kerosene through the reactor for 7 hours at a temperature of 675° F. and a hydrogen gas rate of about 3000 standard cubic feet per barrel. The space velocity was 2 volumes per volume per hour and the reactor pressure was 300 p.s.i.g.

Upon completion of the presulfiding, the reactor was employed for a study of single stage hydrofining. In the first series, the effect of temperature was investigated. Temperatures investigated were 620° F. and 650° F. The liquid hourly space velocities were 2.0 volumes per volume per hour and the hydrogen gas rate was maintained at about 6000 standard cubic feet per barrel. Upon the completion of each run, the reactor effluent was sampled and analyzed for its sulfur, indene, naphthalene-alkylnaphthalene and indenes-Tetralin content. The results are shown in the following table wherein the loss in naphthalenes and the sulfur content of the product obtained upon the hydrofining treatment are set forth as a function of the temperature. The ratio of these values which indicates the selectivity of the process is also set forth. As the example shows, although a 30° increase in temperature resulted in a substantial reduction in sulfur content, this effect was more than offset by the greater degree of naphthalene saturation. The degree of selectivity as defined by the ratio of naphthalene saturation to sulfur in the product was about three times more favorable for naphthalene saturation at the higher temperature.

TABLE 1

Run	Temperature, ° F.	Product Sulfur, p.p.m.	Loss in Naphthalene, percent	Ratio
1	620	55	4.4	0.080
2	650	35	7.8	0.223

EXAMPLE 2

A very substantial temperature rise was observed during the experiments described in Example 1. The temperature rise resulted in peak temperatures which were

25° to 30° in excess of the average temperature in the reactor. To minimize the temperature rise, the reaction was conducted in two stages. This was achieved in the aforedescribed reactor by passing the naphthalene rich stream through the catalyst bed at low temperatures. The product effluent was collected and subsequently hydrofined at a higher temperature; see Example 3. The intermediate product, prior to the second stage of hydrofining, was analyzed and the results are presented in Table 2.

A series of runs were performed simulating the low temperature indene saturation first stage reactor illustrated in the figure. These runs were made at space velocities of 4.3 volumes per volume per hour and a hydrogen to oil ratio of about 5700 standard cubic feet per barrel. The inlet temperatures were varied during the series of runs to achieve average bed temperatures of 350°, 400° and 440° F. The results depicted in Table 2 show that the indenes were saturated throughout the range of conditions investigated and that a minor degree of desulfurization was achieved. No hydrogenation of naphthalenes to Tetralins was observed under these low temperature conditions.

TABLE 2

Run	Temperature, ° F.	Sulfur, p.p.m.	Indenes, percent
Feed		700	12.1
3	350	700	6.1
4	400	600	4.5
5	440	530	2.5

EXAMPLE 3

The products obtained from Example 2 were returned to the reactor for hydrosulfurization at more elevated temperatures. Two runs were performed at 545° and 605°F., space velocities of 2.0 volumes per volume per hour and about 5900 standard cubic feet of hydrogen per barrel of feed. A second set of runs duplicating the temperature and hydrogen gas rate of the preceding at a space velocity of 3.0 volumes per volume per hour were also performed. The results of these runs are summarized in Table 3. These data show that the indene and sulfur content of the feedstock were substantially reduced with only a minor degree of naphthalene saturation.

TABLE 3

Run	Temperature,° F.	Space Velocity, v./v./hr.	Product Sulfur, p.p.m.	Indenes, Percent	Loss in Naph., Percent	Ratio
6	545	2.0	200	1.7	0.5	0.0025
7	605	2.0	55	1.5	3.6	0.066
8	545	3.0	220	1.7	0.1	0.0004
9	605	3.0	89	1.4	2.3	0.025

A comparison of the results from runs 1 and 7 clearly shows the improvement obtainable by the two stage hydrofining of my invention. Although the product sulfur was identical, 55 p.p.m. the single stage resulted in a 22 percent greater saturation of naphthalenes.

The preceding examples are intended solely to illustrate my invention and demonstrate the improvements obtainable therewith. They are not to be construed as unduly limiting of the invention which is intended to be defined by the method steps and their equivalents set forth by the following claims.

I claim:

1. The method for the hydrofining of a naphthalene containing feedstock for the removal of indenes, diolefins and sulfur impurities therefrom which comprises contacting the naphthalene feedstock in a first stage with

hydrogen and a granular hydrofining catalyst at a temperature between about 300° and 550° F. and liquid hourly space velocities between about 1 and 10 volumes per volume per hour to thereby hydrogenate said indene impurities and thereafter contacting the resultant partially purified feedstock with hydrogen and a granular hydrofining catalyst in a second stage at a temperature between about 500° and about 775° F. and a liquid hourly space velocity between about 1 and about 5 volumes per volume per hour to effect removal of the remaining impurities of said feedstock.

2. The method of claim 1 wherein a sulfided composite of cobalt oxide and molybdenum oxide supported on an activated alumina carrier is the hydrofining catalyst for each of said stages.

3. The method of claim 1 wherein said feedstock is supplied to said first stage hydrofining in liquid phase and the intermediate product from said first stage hydrofining is supplied to subsequent hydrofining in vapor phase.

4. The method of claim 3 wherein said intermediate product is withdrawn from said first stage, heated to a temperature between about 500° and about 700° F., and subsequently hydrofined.

5. The method of claim 1 wherein said hydrofining is maintained at substantially isothermal conditions by cooling said feedstock intermediate said hydrofining treatment.

6. A method for the selective hydrofining of a feedstock containing naphthalenes, indenes, sulfur and nitrogen impurities which comprises contacting said feedstock in a first stage with hydrogen and a hydrofining catalyst at

mild hydrogenation conditions including a temperature between about 300° and 550° F. and a liquid hourly space velocity between about 1 and about 10 volumes per volume per hour so as to saturate said indenes and, thereafter, contacting the resultant intermediate product in a second stage with hydrogen and a hydrofining catalyst at more severe conditions, including a temperature between about 500° and 775° F. and a liquid hourly space velocity between about 1 and about 10 volumes per volume per hour.

7. The method of claim 6 wherein a sulfided composite of cobalt oxide and molybdenum oxide on activated alumina is said hydrofining catalyst in said first and second stages.

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