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HYDROCRACKING AND HYDRODESULFURIZATION PROCESS

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ABSTRACT OF THE DISCLOSURE

An improved process for the hydrocracking and hydrodesulfurization of heavy hydrocarbon oils such as residual oils which is characterized by high conversion and efficient sulfur removal. The process involves a first step in which the hydrocarbon oil and hydrogen are reacted at elevated temperature and pressure in the presence of an active particulate hydrodesulfurization catalyst wherein hydrocracking occurs up to about 50% conversion. The reaction product is thereafter reacted in a second step with hydrogen at elevated temperature and pressure in the presence of a less active particulate hydrodesulfurization catalyst wherein hydrocracking is carried to an overall conversion of up to about 80% and sulfur content is reduced to a low level.

BACKGROUND OF THE INVENTION

In the catalytic treatment of heavy hydrocarbon oils to affect hydrocracking and hydrodesulfurization, it is desirable to achieve hydrocracking at high conversion while at the same time achieving as high a degree of sulfur removal as possible. However, solid catalysts having a high level of hydrodesulfurization activity are generally not usable in processes where hydrocracking is carried out at high conversion. For example, degradation products of the heavy hydrocarbon oil formed as a result of the hydrocracking and hydrodesulfurization processes may coat the catalyst particles to thereby render the catalyst inactive. Also, the degradation products may cause agglomeration of the catalyst particles to thereby reduce its surface area as well as to render it inoperable in a so-called "ebullated" catalyst process such as that described in Re. 25,770.

SUMMARY

It is therefore an object of this invention to provide an improved process for the hydrocracking and hydrosulfurization of heavy hydrocarbon oils.

It is another object of this invention to provide a process for hydrocracking heavy hydrocarbon oils to high conversion while achieving a high level of hydrodesulfurization.

Yet other objects and advantages will be apparent to those skilled in the art from the description contained herein.

The foregoing objects are achieved according to the practice of this invention. Broadly, this invention consists of a process for the hydrocracking and hydrodesulfurization of a heavy hydrocarbon oil comprising the steps:

a. Contacting said heavy hydrocarbon oil and hydrogen at elevated temperature and pressure with an active particulate cobalt molybdate on alumina hydrodesulfurization catalyst in a first reaction zone until the degree of hydrocracking reaches up to about 50% conversion; and

b. Contacting said partially hydrocracked and partially desulfurized oil and hydrogen at elevated temperature and pressure with a less active particulate cobalt molybdate on alumina hydrodesulfurization catalyst in a second reaction zone until the overall degree of hydrocracking reaches up to about 80% conversion.

By the practice of this invention, a heavy hydrocarbon oil may be hydrocracked to high conversion while achieving a high level of hydrodesulfurization.

DETAILED DESCRIPTION

When heavy hydrocarbon oils are subjected to a hydrocracking-hydrodesulfurization process, it is desirable to achieve hydrocracking at high conversion while at the same time achieving as high a degree of sulfur removal as possible. A hydrocracking-hydrodesulfurization process is commonly carried out by subjecting a heavy hydrocarbon oil and hydrogen to elevated temperature and pressure in the presence of a particulate hydrodesulfurization catalyst. The heavy hydrocarbon oils that are contemplated for charge stocks in hydrocracking-hydrodesulfurization processes generally are atmospheric or vacuum distillation tower residual petroleum streams containing at least about 25% by volume of hydrocarbons boiling about 975° F. Such hydrocarbon oils also contain sulfur present in the form of refractory compounds. Removal of as much sulfur as possible from the hydrocracked products of such hydrocarbon oils is desirable since the presence of sulfur in said hydrocracked products yields air polluting oxides of sulfur when said products are burned.

Among the more prominent catalysts that may be used for hydrodesulfurization is cobalt molybdate deposited on alumina. As stated above, my invention involves a two step process employing an active cobalt molybdate on alumina hydrodesulfurization catalyst in the first step and a less active cobalt molybdate on alumina hydrodesulfurization catalyst in the second step. I employ as the active hydrodesulfurization catalyst a relatively nonporous, particulate cobalt molybdate deposited on alumina. As the less active hydrodesulfurization catalyst I employ a relatively porous, particulate cobalt molybdate reposited on alumina. I believe that the difference in hydrodesulfurization activity of the two catalysts is due to differences in the average pore sizes, but I do not limit myself thereto. Both catalysts are particulate, the particle sizes being within the ability of one skilled in the art to determine. Generally, the catalyst particles are about 0.1–0.25 inch long and about 0.03–0.04 inch in diameter. However, particle size is not especially critical.

The active hydrodesulfurization catalyst is cobalt molybdate deposited on alumina. The catalyst contains about 3.0–4.0% by weight of CoO and about 13.5–15.0% by weight of MoO_3. The surface area of the catalyst is about 200 $M.^2/g.$ minimum. The pore volume of the catalyst is about 0.50–0.60 cc./g. The pore size distribution is defined as follows:

Pore Size Distribution:	Pore Volume, cc./g.
>40 A. diameter	0.25–0.50
>125 A. diameter (maximum)	0.05

From the above table it is apparent that the active hydrodesulfurization catalyst has small pores, most being in the range of about 40–125 A. diameter.

The less active hydrodesulfurization catalyst is also cobalt molybdate deposited on alumina. The catalyst contains about 3.5–4.0% by weight of CoO and about 14.5–15.5% by weight of MoO_3. The surface area of the catalyst is about 250 $M.^2/g.$ minimum. The pore volume of the catalyst is about 0.75–0.85 cc./g. The pore size distribution is defined as follows:

Pore Size Distribution:	Pore Volume, cc./g.
>250 A. diameter	0.22–0.31
>500 A. diameter	0.18–0.28
>1500 A. diameter	0.12–0.24
>4000 A. diameter	0.06–0.16

It is apparent from the foregoing table that the less active hydrodesulfurization catalyst has greater pore volume and larger average pore diameter than does the active hydrodesulfurization catalyst.

The hydrocracking-hydrodesulfurization process of this invention is carried out at a temperature that is within the range of about 750°–900° F. and preferably within the range of about 800°–850° F. The process is carried out at a pressure that is broadly within the range of about 500–5000 p.s.i.g. and preferably within the range of about 1500–3000 p.s.i.g. The amount of hydrogen used is broadly within the range of about 2,000–15,000 cubic feet at standard temperature and pressure (STP) per barrel of heavy hydrocarbon undergoing the hydrocracking-hydrodesulfurization process. However, it is preferred that about 3,000–10,000 cubic feet (STP) of hydrogen per barrel of heavy hydrocarbon be used. The foregoing temperature and pressure parameters apply to both the first and the second stages of the hydrocracking-hydrodesulfurization process.

In the practice of my invention, the heavy hydrocarbon oil to be subjected to the hydrocracking-hydrodesulfurization process and a suitable amount of hydrogen are brought into contact with the active hydrodesulfurization catalyst in a first reaction zone and subjected to elevated temperature and pressure within the ranges set forth above until the degree of hydrocracking reaches about 40–50% conversion. By definition, the percent conversion is the percent of hydrocarbons boiling above 975° F. that are hydrocracked to hydrocarbons boiling below 975° F. The hydrocracking in the first stage of the process is not allowed to exceed about 50% conversion because, above this level, degradation products present in the reaction mixture cause agglomeration of the active hydrodesulfurization catalyst particles, thereby rendering the catalyst inoperable.

The reaction product, including unreacted hydrogen, is then conducted from the first reaction zone to a second reaction zone containing the less reactive hydrodesulfurization catalyst, and the reaction mixture is subjected to elevated temperature and pressure within the ranges set forth above until the overall degree of hydrocracking reaches about 70–80% conversion. The less active hydrodesulfurization catalyst is not agglomerated by the degradation products present in the reaction mixture and therefore is operable even when the hydrocracking reaches a high conversion.

Thus, by the practice of my invention the heavy hydrocarbon oil is hydrocracked to up to about 50% conversion and a major proportion of the sulfur contained therein is removed in the first stage of the process and, in the second stage of the process, hydrocracking is continued to an overall conversion of up to about 80% while additional sulfur is removed. The overall two stage process of the instant invention therefore permits hydrocracking to high conversion while at the same time a high level of sulfur removal is achieved. Both stages of the instant invention may advantageously be carried out using the so-called "ebullated" or expanded catalyst bed described in Re. 25,770.

A preferred embodiment of my invention may be carried out as follows. A heavy distillation tower residual hydrocarbon oil containing sulfur and greater than 25% by volume of hydrocarbons boiling above 975° F. is mixed with hydrogen in the proportion of about 5000 cubic feet (STP) of hydrogen per barrel of hydrocarbon oil. The mixture is passed upward through a bed of the active cobalt molybdate on alumina hydrodesulfurization catalyst contained in a first closed reactor at such a rate as to cause the catalyst bed to expand, giving a so-called "ebullated" catalyst bed. The temperature within the reactor is maintained within the range of 800°–850° F. and the pressure within the range of 1500–3000 p.s.i.g. The reaction conditions are such as to permit no more than 50% of the hydrocarbons boiling above 975° F. to be converted to hydrocarbons boiling below 975° F. Simultaneous partial hydrodesulfurization also occurs in the first reactor.

The partially hydrocracked and partially hydrodesulfurized hydrocarbon oil and unreacted hydrogen are then removed from the first closed reactor and conducted to a second closed reactor. The hydrocarbon oil-hydrogen mixture is passed upward through a bed of the less active cobalt molybdate on alumina hydrodesulfurization catalyst contained in the second closed reactor at a rate sufficient to cause the catalyst bed to expand to give an "ebullated" bed. The temperature within the reactor is maintained within the range of 800°–850° F. and the pressure within the range of 1500–3000 p.s.i.g. The reaction conditions are such as to permit overall hydrocracking conversion to reach 80%, i.e., 80% of the hydrocarbons boiling above 975° F. that were present in the original residual hydrocarbon oil charge stock are converted to hydrocarbons boiling below 975° F. The hydrocarbon oil simultaneously undergoes further hydrodesulfurization. The final hydrocarbon oil product recovered from the second reactor has undergone overall hydrocracking to 80% conversion in addition to having the sulfur content markedly reduced. There is no appreciable agglomeration of the catalyst in either reactor.

Thus, by the practice of my invention a heavy hydrocarbon oil may be hydrocracked to high conversion while at the same time a high level of sulfur removal by hydrodesulfurization is achieved. In the practice of this invention, a highly active hydrodesulfurization catalyst may be successfully employed in a process where hydrocracking to high conversion is achieved.

While this invention has been illustrated by the presentation of a specific example, it will be understood that the scope of the invention is limited only by the appended claims.

I claim:

1. A process for the hydrocracking and hydrodesulfurization of a heavy hydrocarbon oil, wherein the oil is a distillation tower residual petroleum oil containing at least about 25% by volume of hydrocarbons boiling above 975° F., comprising the steps:

(a) contacting said heavy hydrocarbon oil and hydrogen at a pressure of from about 500 to about 5,000 p.s.i.g. and a temperature of about 750–900° F. with an active particulate cobalt molybdate on alumina hydrodesulfurization catalyst in a first reaction zone until the degree of hydrocracking approaches about 50% conversion, with the oil and hydrogen being passed upward through the catalyst bed at such a rate as to cause the bed to expand and to form an ebullated catalyst bed, and then

(b) contacting said partially hydrocracked and partially desulfurized oil and hydrogen, at temperature and pressure similar to that found in step (a) with a less active particulate cobalt molybdate on alumina hydrodesulfurization catalyst in a second reaction zone until the overall degree of hydrocracking reaches up to about 80% conversion, with the quantity of hydrogen employed ranging from about 2,000 to about 15,000 cubic feet (STP) per barrel of said oil in the hydrocracking-hydrodesulfurization process, wherein the improvement comprises

using a catalyst in step (a) having a pore volume within the range of about 0.50–0.60 cc./g. and the pore size distribution is

Pore Size Distribution:	Pore Vol., cc./g.
>40 A. diameter	0.25–0.50
>125 A. diameter (maximum)	0.05

and using a catalyst in step (b) having a pore volume within the range of about 0.75–0.85 cc./g. and the pore size distribution is

Pore Size Distribution:	Pore Vol., cc./g.
>250 A. diameter	0.22–0.31
>500 A. diameter	0.18–0.28
>1500 A. diameter	0.12–0.24
>4000 A. diameter	0.06–0.16

2. The process of Claim **1** wherein steps (a) and (b) are carried out at a temperature within the range of about 800°–850° F. and a pressure within the range of about 1500–3000 p.s.i.g.

3. The process of Claim **1** wherein the quantity of hydrogen employed is within the range of about 3,000–10,000 cubic feet (STP) per barrel of said hydrocarbon oil.

4. The process of Claim **1** wherein the active hydrodesulfurization catalyst of (a) contains about 3.0–4.0% by weight of CoO and about 13.5–15.0% by weight of MoO_3 and the less active hydrodesulfurization catalyst of (b) contains about 3.5–4.0% by weight of CoO and about 14.5–15.5% by weight of MoO_3.

5. The process of Claim **4** wherein the surface area of the active hydrodesulfurization catalyst of (a) is at least about 200 $M.^2/g.$ and the surface area of the less active hydrodesulfurization catalyst of (b) is at least about 250 $M.^2/g.$

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