SPECIFICATION

TITLE OF THE INVENTION

METHOD OF MANUFACTURING GAS OIL CONTAINING LOW-SULFUR AND LOW-AROMATIC-COMPOUND

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of manufacturing gas oil containing low-sulfur and low-aromatic-compound and, more particularly, it relates to a method of manufacturing gas oil containing low-sulfur and low-aromatic-compound from distilled petroleum.

2. Background Art

In current Japan, gas oil for diesel engines is typically prepared by mixing a desulfurized gas oil fraction obtained by treating straight-run gas oil in an ordinary desulfurizer, a straight-run gas oil fraction, a straight-run kerosene fraction and a gas oil fraction obtained from a cracking facility and normally contains sulfur by 0.1 to 0.2 % by weight. However, the prevalent environmental view in this country requires a further reduction in the concentration of NOx and particulate substances in the diesel engine exhaust gas and it is stipulated by law that the sulfur concentration in gas oil has to be reduced from the current level of 0.2 wt% to as low as 0.05 wt%.

Additionally, it is a popularly accepted theory that aromatic compounds contained in gas oil can give rise to Nox and particulate substances in the diesel engine exhaust gas as they lower the cetane value of gas oil, making a reduction in the concentration of aromatic compounds an urgent problem to be solved. In particular, in view of the fact that cracked gas oil that is drawn out of fluid catalytic cracking facilities and expected to see an ever increasing demand as a basic component of gas oil contains aromatic compounds to a large concentration, any attempt to reduce the aromatic-compound concentration in gas oil should be very significant.

A noble metal type catalyst that can actively hydrogenate aromatic compounds is preferably used for manufacturing gas oil containing low-aromatic-compound. However, since a noble metal type catalyst can be severely poisoned by sulfur compounds and hydrogen sulfide, oil has to be sufficiently desulfurized and hydrogen sulfide produced by the process of desulfurization has to be removed satisfactorily before reducing the concentration of aromatic compounds by means of a noble metal type catalyst.

Thus, currently, the process of manufacturing gas oil containing low-sulfur and low-aromatic-compound proceeds as follows. In the first step of operation, feedstock oil is put into contact with a hydrotreating catalyst in the

presence of hydrogen for desulfurization at high temperature and under high pressure. Then, the product is cooled and the gaseous component is separated from the liquid component to remove any gaseous component before hydrogen sulfide dissolved in the liquid component is stripped off under atmospheric pressure. Thereafter, the obtained oil that contains sulfur compounds to a reduced concentration is put to contact with a noble metal type catalyst to reduce the concentration of aromatic compounds while raising the pressure again and heating the oil with hydrogen gas to a predetermined temperature by means of a heat exchanger (AlChE 1993 Spring National Meeting Preprint, (70e), 5). However, this process requires complicated equipment and is commercially not feasible because of the large plant and equipment investment and a high running cost.

SUMMARY OF THE INVENTION

It is therefore the object of the invention to provide a method of manufacturing gas oil with a sulfur concentration of not higher than 0.05 wt% and a reduced concentration of aromatic compounds from sulfur containing distilled petroleum.

As a result of intensive research efforts, the inventors of the invention have found that gas oil containing low-sulfur and low-aromatic-compound can be produced from

distilled petroleum by means of a two-step hydrotreating process that is conducted under specific conditions.

Thus, according to the present invention, the above object is achieved by providing a method of manufacturing gas oil containing low-sulfur and low-aromatic-compound, said method comprising a first step of putting distilled petroleum to contact with hydrogen gas in the presence of a hydrotreating catalyst to reduce the sulfur concentration to not higher than 0.05 wt% and a second step of reducing the aromatic compound concentration in the presence of a noble metal type catalyst, characterized in that at least a pair of high temperature high pressure gas liquid separators are arranged between the two steps to separate the gaseous and liquid components of distilled petroleum and hydrogen gas or hydrogen containing gas is introduced into the liquid component in each of the separators.

For the purpose of the present invention, distilled petroleum preferably contains sulfur and sulfur compounds to a concentration between 0.1 and 2.0 wt% and has a boiling point between 150 and 400°C. For the purpose of the present invention, distilled petroleum may be distilled oil obtained by distilling crude oil under atmospheric or reduced pressure or by distilling an oil product of fluid catalytic cracking (FCC) or thermal cracking. Any of these different distilled petroleums may be used independently or as a mixture.

For the purpose of the present invention, distilled petroleum is preferably a mixture of distilled oil obtained by distilling an oil product of fluid catalytic cracking (FCC) or thermal cracking and distilled oil obtained by distilling crude oil under atmospheric or reduced pressure. The ratio at which the distilled oil obtained by distilling an oil product of fluid catalytic cracking (FCC) or thermal cracking and the distilled oil obtained by distilling crude oil under atmospheric or reduced pressure are mixed is between 1:99 and 99:1 and preferably between 10:90 and 50:50.

For the purpose of the present invention, desulfurization of distilled petroleum mainly take place in the first step and the concentration of aromatic compounds is reduced in the second step. The operation of separating the gas and liquid components is repeated at least twice between the first step and the second step, and hydrogen gas or hydrogen containing gas is introduced into the separated liquid in order to reduce the concentration of hydrogen sulfide gas dissolved in the liquid.

The hydrotreating operation of the first step is conducted at temperature between 300 and 450°C, preferably between 330 and 400°C, when measured at the outlet of the catalyst layer.

The hydrotreating operation of the first step is conducted under hydrogen partial pressure of between 30 and

150 kg/cm^2, preferably between 50 and 100 kg/cm^2.

In the first step, distilled petroleum is preferably fed at a rate (liquid hourly space velocity-LHSV) of between 0.1 and 10 h^{-1}, more preferably between 0.5 and 6 h^{-1}. In the first step, hydrogen gas is preferably fed at a rate of between 200 and 5,000 scf/bbl, more preferably between 500 and 2,000 scf/bbl, in terms of hydrogen gas/oil ratio.

The hydrotreating catalyst of the first step may be a catalyst normally used for ordinary hydrotreatment of distilled petroleum and realized by using a porous inorganic oxide carrier carrying a hydrogenation active metal. For the purpose of the present invention, materials that can be used for a porous inorganic oxide carrier include alumina, titania, boria, zirconia, silica-alumina, silica-magnesia, alumina-magnesia, alumina-titania, silica-titania, alumina-boria and alumina-zirconia. The use of alumina or silica-alumina is particularly preferable.

Hydrogenation active metals include chromium, molybdenum, tungsten, cobalt and nickel. Any of these metals may be used independently or as a mixture. The use of a mixture of cobalt-molybdenum, nickel-molybdenum or nickel-cobalt is particularly preferable. Any of these metals can lie on the carrier in the form of metal, oxide, sulfide or a mixture thereof. For the purpose of the present

invention, a catalyst realized by using an alumina carrier of carrying thereon active metals of cobalt-molybdenum, nickel-molybdenum or nickel-cobalt is preferably used in the first step.

Any known technique such as impregnation and coprecipitation may be used to make a carrier carry one or more than one active metals. The rate at which the carrier carries one or more than one active metals is between 1 and 30 wt%, more preferably between 3 and 20 wt%, in terms of their respective oxides.

The catalyst may take any form such as that of particulates, tablets, cylindrical columns, trefoils or quatrefoils. The hydrotreating catalyst of the first step may preferably be sulfurized in advance before it is actually put to use.

The hydrotreating reaction column to be used for the first step may be of a fixed bed type, a fluid bed type or an expansive bed type, although a fixed bed type is particularly preferable.

The mode of contact of hydrogen and distilled petroleum in the first step may be that of parallel rising flow, parallel falling flow or counterflow.

For the purpose of the present invention, distilled petroleum is desulfurized in the first step until the sulfur concentration is reduced to not higher than 0.05 wt%.

For the purpose of the present invention, at least a pair of high temperature high pressure gas liquid separators are arranged between the first step and the second step. These separators are connected in series.

A mixture of gas and liquid coming from the first step is fed to the first high temperature high pressure gas liquid separator to separate the mixture into gas and liquid. After introducing hydrogen gas or hydrogen containing gas into the liquid, the latter is fed to the second high temperature high pressure gas liquid separator to separate it further into gas and liquid. Then, hydrogen gas or hydrogen containing gas is introduced again into the obtained liquid before it is fed to the second step of hydrogenation. By repeating at least twice the operation of introducing hydrogen gas or hydrogen containing gas into the liquid produced by the gas/liquid separation process, the hydrogen sulfide concentration in the liquid can be significantly reduced.

All the high temperature high pressure gas liquid separators arranged between the first and second steps are operated for gas/liquid separation at temperature of between 200 and 450°C, preferably between 220 and 400°C, and under pressure of between 30 and 150 kg/cm^2, preferably between 50 and 100 kg/cm^2.

For the purpose of the present invention, hydrogen

gas needs to be pure hydrogen gas, whereas hydrogen containing gas contains hydrogen preferably by not lower than 50 vol%, more preferably not lower than 60 vol%. Hydrogen containing gas is a mixture of a gaseous product of a reaction tower and unreacted hydrogen gas and contains as principal ingredients hydrogen gas, hydrocarbon gas, inert gas and hydrogen sulfide gas. If the gaseous mixture is recirculated for use, the concentration of hydrogen sulfide gas has to be reduced to a predetermined level by treating with amine compounds, or the like.

Preferably pure hydrogen gas is introduced into the liquid produced by the high temperature high pressure gas liquid separators arranged between the first and second steps. If hydrogen containing gas is used instead, the concentration of hydrogen sulfide gas in it is preferably not higher than 2,000 volppm, more preferably not higher than 1,000 volppm. When hydrogen containing gas is introduced into the liquid produced by the last high temperature high pressure gas liquid separator, the concentration of hydrogen sulfide gas in it is preferably not higher than 500 volppm.

The rate at which hydrogen containing gas is introduced into the liquid produced by the high temperature high pressure gas liquid separators is preferably between 200 and 5,000 scf/bbl, more preferably between 500 and 3,000 scf/bbl, in terms of hydrogen/oil ratio.

Since gas and liquid are separated in gas liquid separators at high temperature, a method according to the present invention can provide a separation efficiency much higher than that of a comparable method that carriers out the gas/liquid separating operation at low temperature. Additionally, since hydrogen gas or hydrogen containing gas is introduced at least twice into the liquid product, the concentration of hydrogen sulfide contained in the liquid product is dramatically reduced. Thus, a noble metal type catalyst that can be severely poisoned by sulfur compounds can be used in the second step. Still additionally, with a method according to the present invention, the equipment for reducing the concentration of hydrogen sulfide can be operated without reducing the temperature and the pressure to ambient temperature and the atmospheric pressure respectively.

In the second step, the concentration of aromatic compounds in gas oil is reduced by hydrogenation.

The hydrogenating operation of this second step is conducted at temperature between 200 and 400°C, preferably between 220 and 350°C, when measured at the outlet of the catalyst layer.

The hydrogenating operation of this second step is conducted under pressure between 30 and 150 kg/cm^2, preferably between 50 and 100 kg/cm^2, in terms of the partial

pressure of hydrogen.

In the second step, distilled petroleum is preferably fed at a rate (liquid hourly space velocity-LHSV) of between 0.5 and 10 h^{-1}, more preferably between 1 and 9 h^{-1}.

In the second step, hydrogen gas is preferably fed at a rate of between 200 and 5,000 scf/bbl, more preferably between 500 and 3,000 scf/bbl.

The hydrogenating catalyst of the second step may be a noble metal type catalyst carried on a carrier. For the purpose of the present invention, the noble metal is selected from ruthenium, rhodium, palladium, iridium, osmium, platinum and a mixture thereof, of which ruthenium, palladium and platinum are preferable because of their high hydrogenation potential.

For the purpose of the present invention, materials that can be used for a carrier include zeolites, clay compounds, sedimentary compounds, porous inorganic oxides and a mixture thereof, of which zeolites and clay compounds are preferably used because of their high sulfur resistance properties.

Further, into the catalyst any additives can be added. The preferable ones are boron, phosphorus, vanadium, molybdenum, manganese, nickel, cobalt, iron, copper, tantalum, niobium, silver, tungsten, rhenium, gold, rare

earth metals, and their derivatives.

The carrier can be made to carry any of the active metal by means of a known technique such as impregnation, coprecipitation or ion exchange. The rate at which the carrier carries the selected active metal is between 0.1 and 10 wt%, more preferably between 0.5 and 3 wt%.

The catalyst of the second step may take any form such as that of particulates, tablets, cylindrical columns, trefoils or quatrefoils.

The hydrogenating catalyst of the second step may preferably be treated for hydrogenation in advance before it is actually put to use.

The hydrogenation reaction column to be used for the second step may be of a fixed bed type, a fluid bed type or an expansive bed type, although a fixed bed type is particularly preferable.

The mode of contact of hydrogen and distilled petroleum in the second step may be that of parallel rising flow, parallel falling flow or counterflow.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, the present invention will be described further by way of examples, although it is not limited by the examples in any means.

(Example 1)

As distilled petroleum, a mixture oil containing atmospheric straight distillation gas oil by 80 % and light cycle oil (LCO) obtained from a fluid catalytic cracking (FCC) by 20 % was used and subjected to a two-step hydrogenation process under the conditions listed in Table 1. A pair of high temperature high pressure gas liquid separators were arranged between the first and second steps and hydrogen gas was introduced into the separated liquid products of the separating operations using the separators. The operating conditions of the high temperature high pressure gas liquid separators are also listed in Table 1. The sulfur concentration of the mixture oil was 0.98 wt% and the concentration of aromatic compounds was 39 % when tested with FIA. A commercially available hydrotreating catalyst comprising an aluminum carrier carrying a 5 wt% of CoO and a 15 wt% of MoO_3 was used for the first step. The catalyst was sulfurized in advance before it was actually put to use by a conventional method. The hydrogenating catalyst of the second step was prepared by using acidic Y-type zeolite powder containing SiO_2 and Al_2O_3 to a content ratio of 20, impregnating it with a mixed solution of platinum chloride and palladium chloride to cause it to carry the noble metals, drying it and thereafter baking it at 300°C for three (3) hours. The noble metal content of the catalyst was 0.8 wt%.

Some of the chemical properties of the output oil of the first step and that of the second step are also listed in Table 1. Note that the concentrations of aromatic compounds in Table 1 are those of gas oil when tested with FIA.

(Comparative Example 1)

The distilled petroleum and the catalysts as well as the test conditions of this example were same as their counterparts of Example 1, except that only one high temperature high pressure gas liquid separator was used. The obtained results are also shown in Table 1.

(Comparative Example 2)

The distilled petroleum and the catalysts as well as the test conditions of this example were same as their counterparts of Example 1, except that no high temperature high pressure gas liquid separator was used. In other words, the product of the first step was directly fed to the second step. The obtained results are also shown in Table 1.

[Table 1]

	Example 1	Comparative Example 1	Comparative Example 2
<Conditions for 1st Step>			
Reaction Pressure (kg/cm^2)	55	55	55
Reaction Temperature (°C)	369	369	369
LHSV (h^{-1})	4.5	4.5	4.5
Hydrogen/Oil Ratio (scf/bbl)	1500	1500	1500
<Properties of 1st Step Oil Product>			
Sulfur Content (wt%)	0.033	0.033	0.033
Aromatic Compounds (%)	36	36	36
<Gas Liquid Separation/Gas Mixing Step>			
No.1			
Pressure (kg/cm^2)	55	55	-
Temperature (°C)	369	369	-
Hydrogen Introduction Rate Hydrogen/Oil Rate (scf/bbl)	1500	1500	-
No.2			
Pressure (kg/cm^2)	55	-	-
Temperature (°C)	369	-	-
Hydrogen Introduction Rate Hydrogen/Oil Rate (scf/bbl)	1500	-	-
<Conditions for 2nd Step>			
Reaction Pressure (kg/cm^2)	55	55	55
Reaction Temperature (°C)	300	300	300
LHSV (h^{-1})	1.5	1.5	1.5
Hydrogen/Oil Ratio (scf/bbl)	1500	1500	-
<Properties of 2nd Step Oil Product>			
Sulfur Content (wt%)	0.030	0.031	0.033
Aromatic Compounds (%)	17	24	34

(Example 2)

The distilled petroleum and the catalysts of this example were same as their counterparts of Example 1 but the test conditions as listed in Table 2 were used. The obtained results are shown in Table 2. Note that the concentrations of aromatic compounds in Table 2 are those of gas oil when tested with FIA.

(Comparative Example 3)

The distilled petroleum and the catalysts of this example were same as their counterparts of Example 1 except that only one high temperature high pressure gas liquid separator was used. The test conditions as listed in Table 2 were used. The obtained results are also shown in Table 2.

(Comparative Example 4)

The distilled petroleum and the catalysts of this example were same as their counterparts of Example 1 except that no high temperature high pressure gas liquid separator was used. The test conditions as listed in Table 2 were used. In other words, the product of the first step was directly fed to the second step. The obtained results are also shown in Table 2.

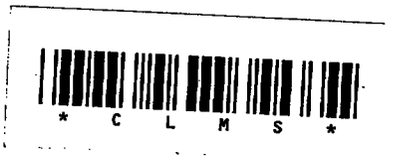
[Table 2]

	Example 2	Comparative Example 3	Comparative Example 4
<Conditions for 1st Step>			
Reaction Pressure (kg/cm^2)	65	65	65
Reaction Temperature (°C)	369	369	369
LHSV (h^{-1})	4.5	4.5	4.5
Hydrogen/Oil Ratio (scf/bbl)	2500	2500	2500
<Properties of 1st Step Oil Product>			
Sulfur Content (wt%)	0.010	0.010	0.010
Aromatic Compounds (%)	35	35	35
<Gas Liquid Separation/Gas Mixing Step>			
No.1			
Pressure (kg/cm^2)	65	65	-
Temperature (°C)	369	369	-
Hydrogen Introduction Rate Hydrogen/Oil Rate (scf/bbl)	2500	2500	-
No.2			
Pressure (kg/cm^2)	65	-	-
Temperature (°C)	369	-	-
Hydrogen Introduction Rate Hydrogen/Oil Rate (scf/bbl)	2500	-	-
<Conditions for 2nd Step>			
Reaction Pressure (kg/cm^2)	65	65	65
Reaction Temperature (°C)	320	320	320
LHSV (h^{-1})	1.5	1.5	1.5
Hydrogen/Oil Ratio (scf/bbl)	2500	2500	-
<Properties of 2nd Step Oil Product>			
Sulfur Content (wt%)	0.009	0.009	0.009
Aromatic Compounds (%)	9	17	30

As seen from the above examples and comparative examples, a hydrotreating method according to the invention is very effective to produce gas oil containing low-sulfur and low-aromatic-compound.

Since at least a pair of high temperature high pressure gas liquid separators are installed between the first and second steps and hydrogen gas or hydrogen

containing gas is introduced into the liquid product of the gas liquid separators to reduce the concentration of hydrogen sulfide contained in the liquid product, one or more than one noble metal type catalysts can be used in the second step to reduce the concentration of aromatic compounds in the produced gas oil.



WHAT IS CLAIMED IS:

1. A method of manufacturing gas oil containing low-sulfur and low-aromatic-compound comprising a first step of putting distilled petroleum to contact with hydrogen gas in the presence of at least one hydrotreating catalyst or a mixture thereof to reduce the sulfur concentration to not higher than 0.05 wt% and a second step of reducing the aromatic compound concentration in the presence of at least one noble metal type catalyst or a mixture thereof, characterized in that at least a pair of high temperature high pressure gas liquid separators are arranged between the two steps to separate the gaseous and liquid components of distilled petroleum and hydrogen gas or hydrogen containing gas is introduced into the liquid component in each of the separators.

2. A method according to claim 1, wherein distilled petroleum is a mixture of distilled oil obtained by distilling an oil product of fluid catalytic cracking (FCC), distilled oil obtained by distilling an oil product of thermal cracking and distilled oil obtained by distilling crude oil under atmospheric or reduced pressure.

3. A method according to claim 1, the gas liquid separators are operated at temperature between 200 and 450°C and under pressure between 30 and 150 kg/cm^2.