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(72) Inventeurs/Inventors:
HABIB, MOHAMMAD M., US;
WINSLOW, PHILIP L., US;
MOORE, RICHARD O., JR., US

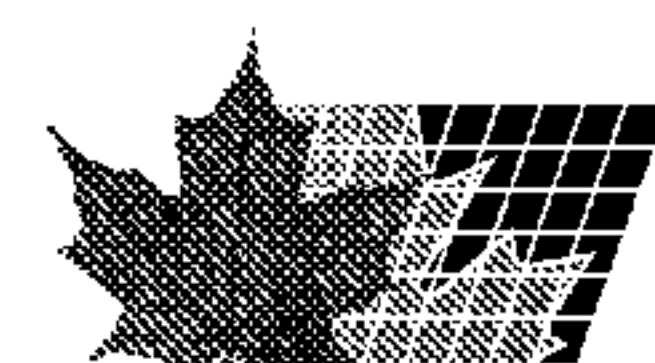
(73) Propriétaire/Owner:
CHEVRON U.S.A. INC., US

(74) Agent: SIM & MCBURNEY

(54) Titre : SYSTÈME DE CATALYSEUR POUR LA COMBINAISON DE L'HYDROTRAITEMENT ET DE
L'HYDROCRAQUAGE ET PROCÉDE POUR ENRICHIIR DES CHARGES D'ALIMENTATION D'HYDROCARBURES
(54) Title: A CATALYST SYSTEM FOR COMBINING HYDROTREATING AND HYDROCRACKING AND A PROCESS
FOR UPGRADING HYDROCARBONACEOUS FEEDSTOCKS

(57) **Abrégé/Abstract:**

A physically intermixed catalyst system comprising two distinctly different catalytic particles, the first of which is a hydrodenitrification and/or hydrodesulfurization catalyst and the second of which is a relatively active hydrocracking catalyst wherein the catalyst particles of both catalytic components are substantially the same size, that is the effective diameter of each catalyst component is substantially the same. The catalyst system of the present invention can be layered with unmixed catalysts. The novel systems of the present invention have been found to provide surprisingly good selectivity for liquid products and stability against catalyst fouling when used in combined hydrotreating and hydrocracking applications, and can therefore be used to provide a stable catalyst system which offers even heat distribution and reactor control in such applications.



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(21) International Application Number: PCT/US93/03317 (22) International Filing Date: 9 April 1993 (09.04.93) (30) Priority data: 07/869,666 16 April 1992 (16.04.92) US (71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventors: HABIB, Mohammad, M. ; 421 Canyon Court, Benicia, CA 94510 (US). WINSLOW, Philip, L. ; 154 Marigold Drive, Hercules, CA 94547 (US). MOORE, Richard, O., Jr. ; 6 Mount Palomar Court, San Rafael, CA 94903 (US).		(74) Agents: AMBROSIUS, James, W. et al.; Chevron Corporation, Post Office Box 7141, San Francisco, CA 94120-7141 (US). (81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: A CATALYST SYSTEM FOR COMBINING HYDROTREATING AND HYDROCRACKING AND A PROCESS FOR UPGRADING HYDROCARBONACEOUS FEEDSTOCKS

(57) Abstract

A physically intermixed catalyst system comprising two distinctly different catalytic particles, the first of which is a hydrotreatment and/or hydrosulfurization catalyst and the second of which is a relatively active hydrocracking catalyst wherein the catalyst particles of both catalytic components are substantially the same size, that is the effective diameter of each catalyst component is substantially the same. The catalyst system of the present invention can be layered with unmixed catalysts. The novel systems of the present invention have been found to provide surprisingly good selectivity for liquid products and stability against catalyst fouling when used in combined hydrotreating and hydrocracking applications, and can therefore be used to provide a stable catalyst system which offers even heat distribution and reactor control in such applications.

-1-

01 A CATALYST SYSTEM FOR COMBINED HYDROTREATING
02 AND HYDROCRACKING AND A PROCESS
03 FOR UPGRADING HYDROCARBONACEOUS FEEDSTOCKS
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11 BACKGROUND OF THE INVENTION
12

13 Field of the Invention
14

15 The present invention relates to a catalyst system and a
16 process for combined hydrotreating and hydrocracking
17 operations in a single reactor bed by contacting a
18 hydrocarbonaceous feedstock with hydrogen under
19 hydrocracking conditions in the presence of an appropriate
20 dual function catalyst system. In particular, the catalyst
21 system and process of this invention relate to a combined
22 denitrification and/or desulfurization hydrotreating process
23 and a hydrocracking process wherein the catalyst system
24 exhibits surprising stability and high selectivity for
25 liquid products boiling in the transportation fuels range.
26 The catalyst system can be tailored to provide previously
27 unavailable flexibility with regard to the selection of the
28 hydrocracking catalyst.

29
30 The dual function catalyst system of the present invention
31 comprises two randomly intermixed particulate catalysts
32 having distinctly different catalytic functions. The first
33 catalyst is a conventional hydrodenitrification and/or
34 hydrodesulfurization catalyst having substantially no

- 2 -

cracking activity. The second catalyst is a conventional zeolitic hydrocracking catalyst. Both catalysts are selected so that they are substantially the same size, that is, the effective diameter for each catalyst particle is substantially the same.

5

The novel catalyst systems of the present invention have been found to provide surprisingly good selectivity for liquid products and stability against catalyst fouling when used in combined hydrotreating and hydrocracking applications, and can therefore be used to provide a stable catalyst system which offers even heat distribution and reactor control in such applications.

10

Objects of Aspects of the Invention

Of the many hydroconversion processes known to the petroleum refining industry, catalytic hydrotreating and catalytic hydrocracking are perhaps the two most widely applied and important. In conventional refining practice, hydrotreating is carried out using a catalyst(s) having as the principle function the removal of nitrogen and/or sulfur, that is catalytic hydrodenitrification and hydrodesulfurization. The product of hydrotreating is then fed to a hydrocracking process unit which uses catalysts having as the principle function hydroconversion to produce liquid products boiling in the transportation fuels range.

15

20

Hydrotreating the feedstock to a hydrocracking process unit is particularly important as nitrogen and sulfur are known to contaminate conventional hydrocracking process catalysts. Thus, hydrotreating is used to lower the nitrogen and sulfur content of the hydrocarbonaceous feedstock stream to an acceptable level before subjecting the hydrocarbons to the

25

-3-

01 complete hydrocracking process. In general, it is desirable
02 to lower the nitrogen content of the hydrocarbon feedstock
03 stream to less than 50 parts per million by weight (ppm),
04 preferably less than about 10 ppm and in many cases for
05 increased catalyst life to a level of less than 2 ppm or
06 even as low as about 0.1 ppm. Similarly, it is generally
07 desirable to lower the sulfur content of the hydrocarbon
08 feedstock stream to less than about 0.5% by weight percent,
09 preferably less than about 0.1%, and in many cases as low as
10 about 1 ppm.

11
12 However, hydrotreating catalysts have various disadvantages.
13 Perhaps the most noted disadvantage is the tendency to foul
14 with coke or other contaminants at an excessive rate. This
15 results in shorter catalyst life than is desirable. As the
16 catalyst fouls or deactivates, the denitrification process
17 temperature must be increased to maintain activity. When
18 the maximum temperature allowed by process and equipment
19 limitations is reached, the catalyst must be replaced or
20 regenerated.

21
22 A variety of measures have been suggested to overcome the
23 problems of catalyst deactivation in hydrotreating systems.
24 For example, U.S. Patent 4,990,243 issued February 5, 1991
25 to Winslow describes a layered catalyst system for
26 hydrodenitrification. The idea behind layered systems is to
27 provide a catalyst system which permits the operator to
28 control the process conditions such as temperature to allow
29 more uniform operations while removing contaminants such as
30 nitrogen. In particular, the layered systems utilize
31 discrete catalyst layers with differing catalysts having
32 differing activity for denitrification and cracking. The
33 first layer is a more active denitrification catalyst which
34 does not induce cracking reactions. The second layer is

-4-

01 more acidic and has higher cracking activity which results
02 in effective conversion of the refractory nitrogen compounds
03 not converted in the first layer.

04

05 U.S. Patent 4,534,852 issued on August 13, 1985 to
06 Washecheck et al. describes a single stage hydrotreating
07 process for converting pitch to conversion process
08 feedstock. According to this process the pitch containing
09 feedstock is contacted with hydrogen and passed downwardly
10 through a hydrotreating zone over a stacked-bed catalyst.
11 The upper bed contains a high activity hydrotreating
12 catalyst, and a separate lower bed contains a high activity
13 desulfurization catalyst. The reaction product is a
14 suitable hydrocracking feedstock.

15

16 U.S. Patent 3,923,638 issued on December 2, 1975 to
17 Bertolacini et al. describes a two-catalyst hydrocracking
18 process. In this process a nitrogen containing feedstock is
19 denitrified in a pretreatment zone using a
20 hydrodenitrification catalyst. The denitrified effluent is
21 passed to a hydrocracking zone. The process can be carried
22 out in a single stage.

23

24 As noted previously the product from hydrotreating can be
25 fed to a hydrocracking process unit. Modern hydrocracking
26 catalysts are generally based on zeolitic materials which
27 may have been adapted by techniques like ammonia ion
28 exchange and various forms of calcination in order to
29 improve the performance of the hydrocracking catalysts based
30 on such zeolites. In nearly all cases, hydrocracking
31 catalysts are formulated to provide varying degrees of
32 cracking activity depending upon the desired product slate.
33 Thus, hydrocracking catalysts which have high activity, and

34

-5-

01 therefore promote the exothermic cracking reactions, may not
02 be suitable for all applications.

03

04 Accordingly, the general approach of catalyst manufacturers
05 has been to offer a family of catalysts tailored in activity
06 for various applications. In other words, operating
07 flexibility is achieved by selecting from a variety of
08 available catalysts the one catalyst which is most suitable
09 for the specific application at hand. However, this
10 solution has created another difficulty. Refiners have
11 found that on occasion the product slate changes which they
12 wish to make are not possible if the choice of available
13 hydrocracking catalysts in inventory does not include the
14 particular catalyst with the activity required to produce
15 the new product slate.

16

17 Thus, it would be desirable to provide a stable
18 hydrotreating catalyst system with high denitrification
19 and/or desulfurization activity which could be used to
20 produce a low nitrogen low sulfur feedstock to a
21 hydrocracking process. It would also be desirable to
22 provide a flexible hydrocracking catalyst system which had
23 high selectivity for liquid products.

24

25 It would be even more desirable to provide a stable catalyst
26 system which could be used to simultaneously carry out
27 combined hydrotreating and hydrocracking to selectively
28 produce liquid products in the transportation fuels boiling
29 range.

30

31 Several attempts have been made to provide dual function
32 combined hydrotreating and hydrocracking processes and
33 catalyst systems.

34

- 6 -

U.S. Patent 4,797,196 issued on January 10, 1989 to Kukes et al. describes a hydrocracking process having intermixed catalysts. In this process, each of the intermixed catalysts has hydrodenitrification and/or hydrodesulfurization activity as well as cracking activity, that is they both have zeolitic components
5 and function to crack the feedstock. Thus, although one of the catalysts is predominantly a hydrotreating catalyst, each catalytic particle is dual functional.

U.S. Patent 4,210,521 issued on July 1, 1980 to Gorrington et al. also describes
10 a dual bed catalytic upgrading process for refractory hydrocarbon stocks. In this process, the refractory feedstock is first catalytically hydrotreated and the hydrotreated product is subsequently cascaded through a hydrocracking zone. The initial hydrotreating step serves to convert sulfur and nitrogen derivatives of hydrocarbons to hydrogen sulfide and ammonia while
15 depositing metal contaminants.

U.S. Patent 4,363,719 issued on December 14, 1982 to Bousquet et al. describes a process to improve the stability of a catalyst to be used for lowering the cloud or turbidity point and the filterability, limit temperature of
20 gas-oils. The catalyst is a composite of a non-acidic hydrodesulfurization catalyst and a non-zeolitic silica-alumina based hydroconversion catalyst.

It is the principal object of an aspect of the present invention to provide a stable catalyst system for combined hydrotreating and hydrocracking process
25 operations with high selectivity for liquid products in the transportation fuels boiling range. This and other objectives of aspects are accomplished by the catalyst system and process summarized below.

- 7 -

SUMMARY OF THE INVENTION

In accordance with an aspect of the invention, there is provided a combined hydrotreating and hydrocracking process which comprises contacting a hydrocarbonaceous feedstock with hydrogen under hydrocracking conditions in the presence of a dual function catalyst system for combined hydrotreating and hydrocracking process operations comprising two randomly intermixed distinctly different particulate catalysts, the first of which is selected from the group consisting of a hydrodenitrification, hydrodesulfurization catalyst, and a combination thereof, having substantially no cracking activity and the second of which is a hydrocracking catalyst, wherein the catalyst particles of both particulate catalysts are substantially the same size, having an effective diameter within a factor of about 4 of each other.

The foregoing catalyst system can be used to carry out combined hydrotreating and hydrocracking processes under typical hydrocracking process conditions.

DETAILED DESCRIPTION OF THE INVENTION

Those familiar with the art related to the present invention will appreciate the full scope of the catalyst system and the process summarized above and be able to practice the present invention over its full scope from a detailed description of the principal features of the catalyst system and process which follows.

The Catalyst System

The dual function catalyst system of the present invention comprises a randomly intermixed combination of at least two discrete particulate catalysts. The first catalyst is a conventional hydrotreating catalyst of the type used to carry out hydrodenitrification and/or hydrodesulfurization

-8-

01 reactions having substantially no cracking activity. Those
02 familiar with the art recognize that such catalysts
03 generally are constituted by a metal from Group VI and a
04 metal from Group VIII placed on a non-acidic oxide such as
05 pure alumina. The commercial catalysts generally fall into
06 one or more of the numerous nickel-molybdenum or cobalt-
07 molybdenum, or nickel-tungsten, or cobalt-tungsten families.
08 The catalytic metals are supported by alumina or other low
09 acidic support material. Such catalysts to be useful in the
10 present invention do not have cracking activity, that is
11 they are non-zeolitic non-acidic catalysts which function to
12 promote hydrodenitrification and/or hydrodesulfurization
13 reactions. Such catalysts are well known in the art.

14

15 The second catalyst particle is a conventional zeolitic
16 hydrocracking catalyst of the type used to carry out
17 hydroconversion reactions to produce transportation fuels.
18 Those familiar with the art recognize that such catalysts
19 are generally based on zeolitic materials which may have
20 been adapted by techniques like ammonia ion exchange and
21 various forms of calcination. In general, suitable zeolitic
22 hydrocracking catalysts comprise a hydrogenation component
23 such as a metal from Group VIB and a metal from Group VIII,
24 their oxides, their sulfides, and mixtures thereof and an
25 acidic support of large pore crystalline zeolitic
26 aluminosilicate.

27

28 One of the zeolites which is considered to be a good
29 starting material for the manufacture of hydrocracking
30 catalysts is the well-known synthetic zeolite Y as described
31 in U.S. Patent 3,130,007 issued April 21, 1964. A number of
32 modifications to this material have been reported one of
33 which is ultrastable Y zeolite as described in U.S.
34 Patent 3,536,605 issued October 27, 1970. To further

-9-

01 enhance the utility of synthetic Y zeolite additional
02 components can be added. For example, U.S. Patent 3,835,027
03 issued on September 10, 1974 to Ward et al. describes a
04 hydrocracking catalysts containing at least one amorphous
05 refractory oxide, a crystalline zeolitic aluminosilicate and
06 a hydrogenation component selected from the Group VI and
07 Group VIII metals and their sulfides and their oxides.

08

09 It has been found that if the two particulate catalysts are
10 selected so that the effective diameter is substantially the
11 same for both the hydrotreating and the hydrocracking
12 catalyst particles it is possible to intermix the two
13 catalysts to provide a system which surprisingly has the
14 beneficial attributes of both hydrotreating and
15 hydrocracking. This is particularly surprising since it is
16 known that conventional hydrotreating catalysts are rapidly
17 fouled by coke buildup, and that conventional zeolitic
18 catalysts catalyze cracking reactions which may cause a heat
19 increase leading to coke formation at the edges of the
20 zeolite particle.

21

22 As used herein, the term "intermixed" means that no effort
23 is made to layer or otherwise segregate the individual
24 hydrotreating catalyst particles from the individual
25 hydrocracking catalyst particles. Thus, the hydrotreating
26 catalyst particles and the hydrocracking catalyst particles
27 are allowed to physically associate with each other in a
28 relatively random manner to form a heterogeneous physical
29 mixture. This can be accomplished prior to or during
30 catalyst loading.

31

32 In order to provide a catalyst system with intermixed
33 hydrotreating and hydrocracking particles which is stable
34 and acceptable for use under conventional hydrocracking

-10-

01 conditions, it has been found that the particle size of each
02 of the catalytic particles must be substantially the same.
03 Although there are a number of catalyst sizing conventions,
04 such as surface to volume ratio, length over diameter ratio,
05 diameter of the circumscribed circle, etc., when comparing
06 catalysts which may have nonuniform shape we have chosen to
07 use the effective diameter of a particle as representative
08 of its size. As used herein the term "effective diameter"
09 for a catalyst particle with a circular cross section means
10 the diameter of that cross section, and for a catalyst
11 particle with a non-circular cross section means the average
12 of the major and minor axes. The important aspect of this
13 parameter is not so much the absolute size of the particles,
14 but rather the relative size of the hydrotreating catalyst
15 particles to the size of the hydrocracking catalyst
16 particles. It is the central feature of the present
17 invention that for the two intermixed catalysts to form the
18 catalyst system of this invention the effective diameter of
19 each must be substantially the same. By "substantially the
20 same" is meant within a factor of about 4 of each other,
21 preferably within a factor of about 2 of each other, and
22 even more preferably within a factor of about 1.5 of each
23 other.

24

25 Therefore, it is not intended that the present invention
26 should be limited by the specific size of the catalysts in
27 question, but rather that the present invention is defined
28 by the relative size of the particles of the two catalysts.

29

30 It is a principal advantage of the present invention that
31 since two conventional catalysts are randomly intermixed to
32 form the catalyst system, it is possible to select a
33 hydrocracking catalyst which under typical conditions would
34 be too active, that is, its heat release would be too great

- 11 -

1 for the equipment available, and to reduce that heat release to within
2 acceptable limitations by combining it with a select hydrotreating catalyst in
3 proportions which give the desired activity. Those familiar with the art will
4 recognize that there are an endless variety of such combinations. In general,
5 the ratio of hydrotreating to hydrocracking catalyst will be within the range of
6 from about 1:20 to about 20:1, preferably within the range of from about 1:10
7 to about 10:1, more preferably within the range of from about 1:5 to about 5:1.

8
9 One such combination which has been found to be particularly effective uses
10 a conventional commercially available nickel-molybdenum hydrotreating
11 catalyst comprising about 3.1 weight percent nickel and about 16 weight
12 percent molybdenum with the balance being phosphorous and alumina; and a
13 Hydrocracking catalyst which is a comulled zeolitic catalyst comprising about
14 17 weight percent alumina binder, about 12 weight percent molybdenum,
15 about 4 weight percent nickel, about 30 weight percent γ -zeolite, and about 30
16 weight percent amorphous silica/alumina. This more general hydrocracking
17 catalyst comprises a Y zeolite having a unit cell size greater than about 24.55
18 Angstroms and a crystal size less than about 2.8 microns together with an
19 amorphous cracking component, a binder, and at least one hydrogenation
20 component selected from the group consisting of a Group VI metal and/or
21 Group viii metal and mixtures thereof.

22
23 In preparing a Y zeolite for use in accordance with the invention herein, the
24 process as disclosed in U.S. patent _____

-12-

01 No. 3,808,326 should be followed to produce a Y zeolite
02 having a crystal size less than about 2.8 microns.

03

04 More specifically, the hydrocracking catalyst suitably
05 comprises from about 30%-90% by weight of Y zeolite and
06 amorphous cracking component, and from about 70%-10% by
07 weight of binder. Preferably, the catalyst comprises rather
08 high amounts of Y zeolite and amorphous cracking component,
09 that is, from about 60%-90% by weight of Y zeolite and
10 amorphous cracking component, and from about 40%-10% by
11 weight of binder, and being particularly preferred from
12 about 80%-85% by weight of Y zeolite and amorphous cracking
13 component, and from about 20%-15% by weight of binder.
14 Preference is given to the use of silica-alumina as the
15 amorphous cracking component.

16

17 The amount of Y zeolite in the catalyst ranges from about
18 5-70% by weight of the combined amount of zeolite and
19 cracking component. Preferably, the amount of Y zeolite in
20 the catalyst compositions ranges from about 10%-60% by
21 weight of the combined amount of zeolite and cracking
22 component, and most preferably the amount of Y zeolite in
23 the catalyst compositions ranges from about 15-40% by weight
24 of the combined amount of zeolite and cracking component.

25

26 Depending on the desired unit cell size, the $\text{SiO}_2/\text{Al}_2\text{O}_3$
27 molar ratio of the Y zeolite may have to be adjusted. There
28 are many techniques described in the art which can be
29 applied to adjust the unit cell size accordingly. It has
30 been found that Y zeolites having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio
31 from about 3 to about 30 can be suitably applied as the
32 zeolite component of the catalyst compositions according to
33 the present invention. Preference is given to Y zeolites

34

-13-

01 having a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from about 4 to about 12,
02 and most preferably having a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from
03 about 5 to about 8.
04

05 The amount of cracking component such as silica-alumina in
06 the hydrocracking catalyst ranges from about 10%-50% by
07 weight, preferably from about 25%-35% by weight. The amount
08 of silica in the silica-alumina ranges from about 10%-70% by
09 weight. Preferably, the amount of silica in the
10 silica-alumina ranges from about 20%-60% by weight, and most
11 preferably the amount of silica in the silica-alumina ranges
12 from about 25%-50% by weight. Also, so-called X-ray
13 amorphous zeolites (i.e., zeolites having crystallite sizes
14 too small to be detected by standard X-ray techniques) can
15 be suitably applied as cracking components according to the
16 process embodiment of the present invention.
17

18 The binder(s) present in the hydrocracking catalyst suitably
19 comprise inorganic oxides. Both amorphous and crystalline
20 binders can be applied. Examples of suitable binders
21 comprise silica, alumina, clays and zirconia. Preference is
22 given to the use of alumina as binder.
23

24 The amount(s) of hydrogenation component(s) in the catalyst
25 suitably range from about 0.5% to about 10% by weight of
26 Group VIII metal component(s) and from about 5% to about 25%
27 by weight of Group VI metal component(s), calculated as
28 metal(s) per 100 parts by weight of total catalyst. The
29 hydrogenation components in the catalyst may be in the
30 oxidic and/or the sulphidic form. If a combination of at
31 least a Group VI and a Group VIII metal component is present
32 as (mixed) oxides, it will be subjected to a sulphiding
33 treatment prior to proper use in hydrocracking.
34

-14-

01 Suitably, the catalyst comprises one or more components of
02 nickel and/or cobalt and one or more components of
03 molybdenum and/or tungsten or one or more components of
04 platinum and/or palladium.
05

06 The hydrocracking catalyst comprises from about 3%-10% by
07 weight of nickel and from about 5%-20% by weight molybdenum.
08 Preferably, the catalyst comprises from about 4%-8% by
09 weight of nickel and from about 8%-15% by weight molybdenum,
10 calculated as metals per 100 parts by weight of total
11 catalyst.
12

13 The effective diameter of the hydrotreating catalyst
14 particles was about 0.1 inch, and the effective diameter of
15 the hydrocracking catalyst particles was also about 0.1
16 inch. The two catalysts are intermixed in a weight ratio of
17 about 1.5:1 hydrotreating to hydrocracking catalyst.
18

19 The catalyst system of the present invention can be used in
20 a variety of configurations. For example, the dual function
21 system of this invention can be layered with unmixed
22 hydrotreating and/or hydrocracking catalysts. In a
23 preferred configuration a single reactor may contain up to
24 four beds, up to about 60% by volume of the first bed being
25 unmixed hydrotreating catalyst, from about 10% by volume of
26 the second bed being the catalyst system of the present
27 invention, up to about 50% by volume of the third bed being
28 unmixed hydrocracking catalyst, and up to about 40% by
29 volume of the fourth bed being unmixed hydrotreating
30 catalyst.
31

32 Having described in detail the catalyst system which is used
33 in the process of the present invention, it is appropriate
34 to consider the second aspect of the present process.

-15-

01 Process Conditions

02

03 The process of the present invention is a combined
04 hydrotreating and hydrocracking process which comprises
05 contacting a hydrocarbonaceous feedstock with hydrogen under
06 typical hydrocracking conditions in the presence of the dual
07 function catalyst system detailed above.

08

09 Representative feedstocks include petroleum crude oils,
10 topped or reduced crude oils, solvent deasphalted oils,
11 distillates, etc. Preferred feedstocks include crude
12 petroleum and atmospheric and vacuum towered bottoms. These
13 feedstocks generally have boiling range above about 200°F
14 and generally have a boiling range between 350°F and about
15 1050°F. More specifically these feedstocks include heavy
16 distillates, heavy straight run gas oils and heavy cracked
17 cycle oils, as well as fluidized catalytic cracking unit
18 feedstocks.

19

20 The hydrocarbonaceous feedstock is contacted with hydrogen
21 in the presence of the catalyst system under upgrading
22 conditions which generally include a temperature in the
23 range of from about 500°F to about 900°F, preferably between
24 about 650°F and about 850°F; a pressure of from about 500
25 pounds per square inch absolute (psia) to about 3,500 psia,
26 preferably from about 1,000 psia to about 3,000 psia; and a
27 liquid hourly space velocity (LHSV) of from about 0.1 to
28 about 6.0, preferably from about 0.5 to about 4; and an oil
29 to gas ratio of from about 2,000 standard cubic feet per
30 barrel (scf/bbl) to about 10,000 scf/bbl, preferably from
31 about 3,000 scf/bbl to about 6,000 scf/bbl.

32

33 With the preferred catalyst system described above it has
34 been found that preferred process conditions include

- 16 -

1 contacting a hydrocarbonaceous feedstock with hydrogen in the presence of
2 the physically intermixed catalyst system under hydrocracking conditions
3 comprising a pressure of about 2,300 psia, a gas to oil ratio at from about
4 4,000 scf/bbl to about 5,000 scf/bbl, a LHSV of about 1.0, and a temperature
5 in the range of from about 680°F to about 800°F.

6

7 These and other specific applications of the catalyst system and process of
8 the present invention are illustrated in the following example.

9

10

EXAMPLE

11

12 The following Example illustrates the efficacy of the present invention.

13

14 A dual catalyst system was prepared by physically intermixing a commercially
15 available nickel-molybdenum hydrotreating catalyst comprising about 3.1
16 weight percent nickel and about 16 weight percent molybdenum with the
17 balance being phosphorous and alumina; and a zeolitic hydrocracking catalyst
18 which is a comulled zeolitic catalyst comprising about 17 weight percent
19 alumina binder, about 12 weight percent molybdenum, about 4 weight percent
20 nickel, about 30 weight percent Y-zeolite, and about 30 weight percent
21 amorphous silica/alumina. This hydrocracking catalyst was prepared by the
22 multi-step process wherein Solution "A" was prepared by dissolving 160.6 g
23 nickel nitrate hexa hydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 70 cc deionized

-17-

01 water and then adding about 25 g concentrated nitric acid
02 (70% HNO_3).
03

04 Solution "B" was a molybdenum solution prepared by stirring
05 and filtering a mixture composed of 26.5 weight percent
06 concentrated aqueous NH_4OH , 28.9 weight percent MoO_3 ,
07 balance deionized water.
08

09 A solid mixture was prepared by mixing 174.7 grams alumina
10 powder, 293.8 grams $\text{SiO}_2/\text{Al}_2\text{O}_3$ powder, and 303.8 grams ultra
11 stable Y zeolite powder in a sigma-blade mixer for 5 minutes
12 at about 150°F mixer jacket temperature. To the solid
13 mixture was then added about 150 cc of deionized water, and
14 the mixture mixed an additional 5 minutes. Solution "A" was
15 then added to the wet solid mixture, and the mixing was
16 continued for an additional 35 minutes.
17

18 483.1 grams of Solution "B" were then dripped into the wet
19 solid mixture over a 5-minute period. 70 cc deionized water
20 were added, and the wet solid mixture was mixed for an
21 additional 15 minutes.
22

23 The wet mixture was extruded in a 2-inch Bonnot extruder.
24 The extrudates were dried in a preheated oven at 320°F for
25 1 hour. They were then heated to 950°F at 288°F/hr in
26 10 com dry air, held for 1 hour at 950°F, and then cooled to
27 room temperature.
28

29 The effective diameter of the hydrotreating catalyst
30 particles was about 0.1 inch, and the effective diameter of
31 the hydrocracking catalyst particles was also about 0.1
32 inch. The two catalysts are intermixed in a weight ratio of
33 about 1.5:1 hydrotreating to hydrocracking catalyst.
34

-18-

01 A feedstock of heavy gas oil having the following
02 characteristics was contacted with above dual catalyst
03 system in the presence of hydrogen:
04

05 API Gravity - 21.0
06 Nitrogen - 2520 ppm
07 Sulfur - 0.8 weight percent
08 D2887 Simulated Distillation
09 St - 380°F
10 50% - 742°F
11 EP - 952°F
12

13 The process conditions were maintained as follows:
14

15 1.0 LHSV
16 2,300 psig total pressure
17 5,500 scf/bbl gas rate
18 680°F-800°F temperature range
19

20 At a target product composition of 1.0 ppm nitrogen and 10
21 ppm sulfur, the dual catalyst system resulted in a 17°F
22 higher activity and 80% improvement in catalyst life
23 relative to a conventional layered catalyst system
24 comprising 60 volume percent of a commercial zeolitic
25 catalyst and 40 volume percent of a commercial nonzeolitic
26 silica/alumina catalyst.
27

28 There are numerous variations on the present invention which
29 are possible in light of the teachings and example
30 supporting the present invention. It is therefore
31 understood that within the scope of the following claims,
32 the invention may be practiced otherwise than as
33 specifically described or exemplified herein.
34

WHAT IS CLAIMED IS:

1. A combined hydrotreating and hydrocracking process which comprises contacting a hydrocarbonaceous feedstock with hydrogen under hydrocracking conditions in the presence of a dual function catalyst system for combined hydrotreating and hydrocracking process operations comprising two randomly intermixed distinctly different particulate catalysts, the first of which is selected from the group consisting of a hydrodenitrification, hydrosulfurization catalyst, and a combination thereof, having substantially no cracking activity and the second of which is a hydrocracking catalyst, wherein the catalyst particles of both particulate catalysts are substantially the same size, having an effective diameter within a factor of about 4 of each other.

5

10
2. A process according to claim 1, wherein the hydrocarbonaceous feedstock is contacted with hydrogen in the presence of the catalyst system under upgrading conditions comprising a temperature in the range of from about 500°F to about 900°F; a pressure of from about 500 psia to about 3,500 psia; a LHSV of from about 0.1 to about 6.0; and an oil to gas ratio of from about 2,000 scf/bbl to about 10, 000 scf/bbl.

15

20
3. A process according to claim 1, wherein the hydrocarbonaceous feedstock is contacted with hydrogen in the presence of the catalyst system under upgrading conditions comprising a temperature in the range of from about 650°F and about 850°F; a pressure of from about 1,000 psia to about 3,000 psia; a LHSV from about 0.5 to about 4; and oil to gas ratio of from about 3,000 scf/bbl to about 6,000 scf/bbl.

25

4. A process according to claim 1, wherein said hydrocracking conditions comprise a pressure of about 2,300 psia, a gas to oil ratio at about 4,000 scf/bbl to about 5,000 scf/bbl, a LHSV of about 1.0, and a
5 temperature in the range of from about 680°F to about 800°F.
5. A process according to claim 3, wherein the hydrocracking catalyst of the catalyst system comprises a Y zeolite having a unit cell size greater than about 24.55 Angstroms and a crystal size less than about 2.8
10 microns together with an amorphous cracking component, a binder, and at least one hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof.