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Superintendencia de Industria y Comercio
E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 04-001078- -00007-0000

Fecha: 2007-11-16 17:39:44 Dep. 2020 NUECREACIONES
Tra. 11 PATENTILYI Eve: 379 FASENACIONALII
Act 444 RESPUESTA RQUE Folios: 13

Trámite : 002 Evento : 001 Actuación : 444

Referencia : Expediente No. 04001078
Asunto : Solicitud de patente para: "REDUCCION DEL
AZUFRE EN LA GASOLINA EN EL CRAQUEO
CATALITICO FLUIDO".
Solicitante : W.R. GRACE & CO.-CONN. y EXXONMOBIL
RESEARCH & ENGINEERING COMPANY
Fecha de la : 8 de Enero de 2004.
Solicitud

1. Yo, Emilio FERRERO, obrando como apoderado del solicitante en el asunto antes identificado, me refiero al Oficio No. 10202 notificado por fijación en lista del 24 de Agosto de 2007.

2. Mediante el Oficio No. 10202 se puso en conocimiento del solicitante el informe del examen de fondo que contiene las observaciones hechas por su Despacho sobre la presente solicitud de patente. Atiendo a las observaciones de la manera siguiente:

3. Evaluación de la novedad:

Su Despacho afirma que el documento D1 (US 4728416) afecta la novedad de las reivindicaciones 1 a 13 de la presente invención debido principalmente a:

"Su Despacho considera que la solicitud en estudio no parece tener alguna característica novedosa comparándolo con el proceso de craqueo FCC revelado en D1 ya que este proceso también considera

una unidad de craqueo de hidrocarburos para obtener livianos como por ejemplo, gasolina, donde dicha unidad contiene un catalizador que favorece la reacción química; además en D1 el catalizador también es recirculado para regenerarlos y se incorpora una composición que contenga vanadio en la corriente de alimentación de hidrocarburos de forma que la concentración de vanadio sobre el catalizador aumenta de la misma manera que en la solicitud pues en D1 se divulga el intervalo de 1500 a 6000 ppm que es abarcado por el intervalo de la solicitud (100 a 20000 ppm)".

4. Modificación a una solicitud en trámite:

Con el objeto de superar la anterior observación y de conformidad con lo establecido en el artículo 34 de la Decisión 486, que permite al solicitante en cualquier momento del trámite efectuar modificaciones, sin ampliar el objeto de la invención inicialmente solicitado, me permito presentar un nuevo capítulo reivindicatorio, que comprende 13 reivindicaciones, el cual cumple a cabalidad con el requisito de novedad.

5. Argumentos en favor de la novedad de la solicitud en estudio:

Como se indicó anteriormente, el capítulo reivindicatorio se modificó de tal forma, que la presente invención ahora reivindica un proceso para reducir el contenido de azufre de productos

líquidos, que incluyen gasolina y productos de craqueo de destilado medio, obtenidos durante un proceso FCC.

De acuerdo con el proceso de la invención, un compuesto que consiste esencialmente en por lo menos un compuesto que contiene vanadio se agrega a una fuente de alimentación de hidrocarburo líquido para incrementar selectivamente la concentración de vanadio en la fuente de alimentación. La fuente de alimentación enriquecida con vanadio es posteriormente cargada en una unidad FCC que opera bajo condiciones de régimen estacionario para poner en contacto un catalizador de craqueo FCC *in situ* con una alta concentración de vanadio, expresada como vanadio elemental.

La referencia D1 (Patente US 4.728.416) revela un proceso mejorado para obtener catalíticamente craqueado una alimentación de gas oil para obtener productos de nafta de un número de octanos mejorado.

El proceso comprende introducir una cantidad suficiente de fuente de alimentación pesada con la alimentación de gas oil que contiene TANTO los metales níquel como vanadio en la zona de craqueo de un FCCU para elevar el contenido de ambos metales níquel y vanadio sobre el catalizador. Ver columna 3, líneas 25-26.

De lo anterior se puede concluir que D1 no describe ni enseña de ninguna manera, el agregar un compuesto que consista esencialmente en por lo menos un compuesto de vanadio a la fuente de alimentación para incrementar selectivamente solo el contenido de vanadio sobre el catalizador.

Además, la referencia D1 no menciona nada con respecto a la reducción de azufre de **productos líquidos** producidos durante el proceso FCC. Un proceso FCC típico produce tanto gas H_2S como **productos que contienen azufre líquido**.

Sin embargo, mi representada argumenta que la presente invención es novedosa porque los inventores encontraron que la presencia de un alto contenido de vanadio en la alimentación durante el proceso de craqueo catalítico, cambia inesperadamente el contenido de azufre presente en los **productos líquidos** a un contenido inferior, produciendo de esta manera un producto líquido que tiene un contenido de azufre reducido comparado con los productos líquidos producidos durante un proceso FCC convencional.

Por lo tanto, el nuevo capítulo reivindicatorio de la presente invención sí es novedoso con respecto a D1, gracias a las diferencias significativas arriba citadas.

6. Conclusión:

De conformidad con los argumentos arriba expuestos y con el nuevo capítulo reivindicatorio que se presenta con este escrito se puede concluir que la presente invención, es novedosa y posee altura inventiva con respecto a D1.

Puesto que se han atendido a cabalidad las observaciones hechas por su Despacho sobre la presente solicitud de patente, respetuosamente solicito se continúe con su tramitación.

7. Anexos:

- Nuevo pliego reivindicatorio que comprende 13 reivindicaciones.
- Formulario para modificaciones.
- Recibo por valor de \$99.000 por concepto de modificaciones en solicitud pendiente.

Bogotá,
Señora Jefe,



EMILIO FERRERO

T.P.A. No. 31.929

FORMULARIO UNICO DE CORRECCIONES Y MODIFICACIONES

1

SOLICITUD DE:

Corrección de Error Material



Modificación a una solicitud

2

SOLICITANTE**Nombre: W. R. GRACE & CO.-CONN.
y EXXONMOBIL RESEARCH
& ENGINEERING COMPANY**Sociedades constituidas y existentes bajo las leyes
de los Estados de Connecticut y Virginia, Estados
Unidos de América.Dirección: 7500 Grace Drive,
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y

3225 Gallows Road,
Fairfax,
Virginia 22037,
Estados Unidos de AméricaDomicilio: Columbia
Maryland,
Estados Unidos de América

y

Fairfax
Virginia,
Estados Unidos de América

Respectivamente.

Teléfono: 546 09 70 **Fax:** 249 40 70
E-mail: clientes@cavelier.com**IDENTIFICACION**

C.C.



NIT



C.E.



Otro



Número: _____

3

**REPRESENTANTE
O APODERADO****Nombre:** Emilio FERRERO**Dirección:** Carrera 4ª No. 72-35**Teléfono:** 347 36 11 **Fax:** 217 92 11**E-mail:** cavelier@cavelier.com**IDENTIFICACION**

C.C.



NIT



C.E.



Otro



Número: 438.019 TP 31.929

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Número de expediente: 04.001.078

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Descripción de la corrección o modificación solicitada:Presento nuevo capítulo reivindicatorio compuesto por 13 reivindicaciones con el fin de atender las
observaciones del examen de fondo.

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Comprobante de pago No. 07-88.552 **Fecha:** 29 de Octubre de 2007

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Anexos

- ☒ Comprobante de pago de la tasa
- ☐ Poderes, si fuere el caso
- ☐ Documento que acredita la existencia y representación legal de las partes, cuando sean personas jurídicas.

8

NOMBRE: EMILIO FERRERO

FIRMA: 

C.C. 438.019 de Usaquén T.P.A. 31.929

0 MGT

REIVINDICACIONES

1. Un proceso para reducir el contenido de azufre de productos de craqueo líquido de un proceso de craqueo catalítico fluido (FCC) en el cual una alimentación de hidrocarburo pesado que comprende compuestos de organoazufre es catalíticamente craqueado a productos más ligeros mediante el contacto en un proceso de craqueo de recirculación de catalizador cíclico con un inventario de catalizador de equilibrio de craqueo catalítico fluidizable circulante, el proceso comprende:

(i) suministrar una corriente de alimentación de hidrocarburo pesado sustancialmente líquido que comprende por lo menos un compuesto de órgano azufre como una impureza;

(ii) introducir una corriente de alimentación de hidrocarburo en la unidad del reactor FCC que opera bajo condiciones de craqueo catalítico y que comprende un inventario circulante de una composición de catalizador en equilibrio;

(iii) remover una porción del inventario de catalizador en equilibrio de la unidad del reactor FCC mientras se rempazan todos los inventarios de catalizador en equilibrio removidos de la unidad con el catalizador fresco para crear un ambiente de régimen estacionario dentro de la unidad del reactor FCC;

(iv) poner en contacto la corriente de alimentación de hidrocarburo con un compuesto que consiste esencialmente de por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar selectivamente la concentración de vanadio en o sobre el inventario de catalizador en equilibrio por aproximadamente 100 a aproximadamente 20.000ppm

con relación a la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador en equilibrio;

- (v) poner en contacto el inventario de catalizador en equilibrio en la unidad del reactor FCC con la corriente de alimentación de hidrocarburo que contiene vanadio bajo un ambiente de régimen estacionario para producir un efluente de la zona de craqueo que comprende productos craqueados líquidos, incluyendo gasolina, que tiene un contenido de azufre reducido.

2. El proceso de la reivindicación 1 que comprende además producir simultáneamente un coque que contiene catalizador de gasto y los hidrocarburos enjuagables en la etapa (iii).

3. El proceso de la reivindicación 2 que comprende además

(i) descargar y separar la mezcla de efluente en una fase de vapor rica en producto craqueado y una fase rica en sólido que comprende catalizador de gasto;

(ii) remover la fase de vapor como un producto y fraccionar el vapor para formar productos de craqueo líquido, que incluyen gasolina, que tienen un contenido de azufre reducido.

4. El proceso de la reivindicación 1 en donde el compuesto de vanadio se selecciona del grupo que consiste de amonio orto-, piro o meta vanadatos, óxidos de vanadio hidratados, ácidos vanádicos, complejos de vanadio organometálico, sulfato de vanadio, sulfato de vanadil, nitrato de vanadio, haluro de vanadio y oxihaluros y mezclas de estos.

5. El proceso de la reivindicación 4 en donde el compuesto de vanadio se selecciona del grupo que consiste de oxalato de vanadio, sulfato de vanadio, naftenato de vanadio, haluros de vanadio y mezclas de estos.

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6. El proceso de la reivindicación 1 en donde la corriente de alimentación de hidrocarburo es puesta en contacto con el compuesto de vanadio en una cantidad suficiente para incrementar selectivamente la concentración del vanadio en o sobre el inventario de catalizador en equilibrio mediante aproximadamente 300 a aproximadamente 5000 ppm con relaciona la cantidad de vanadio inicialmente presente en o sobre el catalizador de craqueo.

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7. El proceso de la reivindicación 6 en donde la corriente de alimentación de hidrocarburo se ponen en contacto con el compuesto de vanadio en una cantidad suficiente para incrementar selectivamente la concentración del vanadio en o sobre el inventario de catalizador en equilibrio mediante aproximadamente 500 a aproximadamente 2000 ppm con relaciona la cantidad de vanadio inicialmente presente en o sobre el catalizador de craqueo.

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8. El proceso de la reivindicación 1 en donde el catalizador de craqueo comprende una zeolita de tamaño de poro grande.

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9. El proceso de la reivindicación 8 en donde la zeolita de tamaño de poro grande comprende un faujasita.

10. El proceso de la reivindicación 1 en donde la alimentación de hidrocarburo comprende además vanadio como una impureza.

11. El proceso de la reivindicación 10 en donde la alimentación de hidrocarburo
5 comprende además níquel como una impureza.

12. Un proceso mejorado para el craqueo catalítico de una fuente de alimentación de hidrocarburo que contiene por lo menos un compuesto de azufre orgánico que comprende poner en contacto en un reactor de craqueo catalítico fluido (FCC) un inventario del catalizador en equilibrio de craqueo catalítico fluido, removiendo una porción del inventario del catalizador aunque remplazando la misma cantidad de la composición de catalizador fresco para suministrar un ambiente de régimen estacionario dentro del reactor FCC, la mejora comprende:

15 (i) poner en contacto la alimentación de hidrocarburo con un compuesto de material que consiste esencialmente de por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar selectivamente la concentración del vanadio en o sobre el inventario de catalizador en equilibrio por aproximadamente 100 a aproximadamente 20000ppm con
20 relación a la cantidad del vanadio inicialmente presente el o sobre el inventario de catalizador en equilibrio.

(ii) poner en contacto de inventario de catalizador en equilibrio con la alimentación de hidrocarburo que contiene vanadio en una unidad del reactor FCC bajo un ambiente de régimen estacionario para producir un
25 efluente de zona de craqueo que comprende productos craqueados

líquidos que incluyen gasolina, que tiene un contenido de azufre reducido.

13. El proceso de la reivindicación 3 en donde el proceso comprende además
5 las etapas adicionales de

(i) enjuagar la fase de catalizador de gasto rico en sólidos para remover los hidrocarburos ocluidos provenientes del catalizador,

10 (ii) transportar los catalizadores enjuagados del enjuagador a un regenerador de catalizador;

(iii) regenerar el catalizador enjuagado al ponerlo en contacto con gas que contiene oxígeno para producir catalizador regenerado; y

(iv) reciclar el catalizador regenerado a la unidad de craqueo para poner en contacto cantidades adicionales de alimentación de hidrocarburo pesado.

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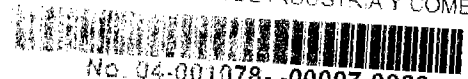
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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800178089-2

RECIBO OFICIAL DE CAJA : 07 - 88.552
FECHA : OCTUBRE 29 DE 2007

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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Lib. 11 PATENTISMO Eje: 379 FASENACIONALI
Art. 444 RESOLUTAREQUE Folios: 13

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	48825371	29/10/2007	46,831,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03	CAMBIO DE MODALIDAD Y MODIFICA	
		12 MARCAS Y LEMAS COMERCIALES	99,000.00
		TOTAL :	\$ 99,000.00

NOVENTA Y NUEVE MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

0010:14101-842-002-2

<http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=US6482315&F=1&RPN=WO012...> 21/12/2007



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(12) **United States Patent**
Roberie et al.

(10) **Patent No.:** **US 6,482,315 B1**
(45) **Date of Patent:** **Nov. 19, 2002**

(54) **GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING**

(75) Inventors: **Terry G. Roberie**, Ellicott City, MD (US); **Ranjit Kumar**, Clarksville, MD (US); **Michael Scott Ziebarth**, Columbia, MD (US); **Wu-Cheng Cheng**, Ellicott City, MD (US); **Xinjin Zhao**, Woodbine, MD (US); **Nazeer Bhore**, Gaithersburg, MD (US)

(73) Assignee: **W.R. Grace & Co.-Conn.**, Columbia, MD (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/649,627**

(22) Filed: **Aug. 28, 2000**

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/399,637, filed on Sep. 20, 1999.

(51) Int. Cl.⁷ **C10G 29/04**

(52) U.S. Cl. **208/249; 208/248; 208/208 R**

(58) Field of Search **208/249, 248, 208/208 R**

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Primary Examiner—Nadine G. Norton

(74) *Attorney, Agent, or Firm*—Beverly J. Artale

(57) **ABSTRACT**

The sulfur content of liquid cracking products, especially the cracked gasoline, of the catalytic cracking process is reduced by the use of a sulfur reduction additive comprising a non-molecular sieve support containing a high content of vanadium. Preferably, the support is alumina. The sulfur reduction catalyst is used in the form of a separate particle additive in combination with the active catalytic cracking catalyst (normally a faujasite such as zeolite Y) to process hydrocarbon feedstocks in the fluid catalytic cracking (FCC) unit to produce low-sulfur gasoline and other liquid products.

26 Claims, No Drawings

GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part to application Ser. No. 09/399,637, filed Sep. 20, 1999.

FIELD OF THE INVENTION

This invention relates to the reduction of sulfur in gasoline and other petroleum products produced by a catalytic cracking process. The invention provides a catalytic composition for reducing product sulfur and a process for reducing product sulfur using this composition.

BACKGROUND OF THE INVENTION

Catalytic cracking is a petroleum refining process which is applied commercially on a very large scale. A majority of the refinery gasoline blending pool in the United States is produced by this process, with almost all being produced using the fluid catalytic cracking (FCC) process. In the catalytic cracking process heavy hydrocarbon fractions are converted into lighter products by reactions taking place at elevated temperature in the presence of a catalyst, with the majority of the conversion or cracking occurring in the vapor phase. The feedstock is thereby converted into gasoline, distillate and other liquid cracking products as well as lighter gaseous cracking products of four or less carbon atoms per molecule. The gas partly consists of olefins and partly of saturated hydrocarbons.

During the cracking reactions some heavy material, known as coke, is deposited onto the catalyst. This reduces the activity of the catalyst and regeneration is desired. After removal of occluded hydrocarbons from the spent cracking catalyst, regeneration is accomplished by burning off the coke to restore catalyst activity. The three characteristic steps of the catalytic cracking can be therefore be distinguished: a cracking step in which the hydrocarbons are converted into lighter products, a stripping step to remove hydrocarbons adsorbed on the catalyst and a regeneration step to burn off coke from the catalyst. The regenerated catalyst is then reused in the cracking step.

Catalytic cracking feedstocks normally contain sulfur in the form of organic sulfur compounds such as mercaptans, sulfides and thiophenes. The products of the cracking process correspondingly tend to contain sulfur impurities even though about half of the sulfur is converted to hydrogen sulfide during the cracking process, mainly by catalytic decomposition of non-thiophenic sulfur compounds. The distribution of sulfur in the cracking products is dependent on a number of factors including feed, catalyst type, additives present, conversion and other operating conditions but, in any event a certain proportion of the sulfur tends to enter the light or heavy gasoline fractions and passes over into the product pool. With increasing environmental regulation being applied to petroleum products, for example in the Reformulated Gasoline (RFG) regulations, the sulfur content of the products has generally been decreased in response to concerns about the emissions of sulfur oxides and other sulfur compounds into the air following combustion processes.

One approach has been to remove the sulfur from the FCC feed by hydrotreating before cracking is initiated. While highly effective, this approach tends to be expensive in terms of the capital cost of the equipment as well as operationally

since hydrogen consumption is high. Another approach has been to remove the sulfur from the cracked products by hydrotreating. Again, while effective, this solution has the drawback that valuable product octane may be lost when the high octane olefins are saturated.

From the economic point of view, it would be desirable to achieve sulfur removal in the cracking process itself since this would effectively desulfurize the major component of the gasoline blending pool without additional treatment. Various catalytic materials have been developed for the removal of sulfur during the FCC process cycle, but, so far most developments have centered on the removal of sulfur from the regenerator stack gases. An early approach developed by Chevron used alumina compounds as additives to the inventory of cracking catalyst to adsorb sulfur oxides in the FCC regenerator; the adsorbed sulfur compounds which entered the process in the feed were released as hydrogen sulfide during the cracking portion of the cycle and passed to the product recovery section of the unit where they were removed. See Krishna et al, *Additives Improve FCC Process*, Hydrocarbon Processing, November 1991, pages 59-66. The sulfur is removed from the stack gases from the regenerator but product sulfur levels are not greatly affected, if at all.

An alternative technology for the removal of sulfur oxides from regenerator stack gases is based on the use of magnesium-aluminum spinels as additives to the circulating catalyst inventory in the FCCU. Under the designation DESOXTM used for the additives in this process, the technology has achieved a notable commercial success. Exemplary patents disclosing this type of sulfur removal additives include U.S. Pat. Nos. 4,963,520; 4,957,892; 4,957,718; 4,790,982 and others. Again, however, product sulfur levels are not greatly reduced.

A catalyst additive for the reduction of sulfur levels in the liquid cracking products was proposed by Wormsbecher and Kim in U.S. Pat. Nos 5,376,608 and 5,525,210, using a cracking catalyst additive of an alumina-supported Lewis acid for the production of reduced-sulfur gasoline but this system has not achieved significant commercial success.

In application Ser. No. 09/144,607, filed Aug. 31, 1998, catalytic materials are described for use in the catalytic cracking process which are capable of reducing the content of the liquid products of the cracking process. These sulfur reduction catalysts comprise, in addition to a porous molecular sieve component, a metal in an oxidation state above zero within the interior of the pore structure of the sieve. The molecular sieve is in most cases a zeolite and it may be a zeolite having characteristics consistent with the large pore zeolites such as zeolite beta or zeolite USY or with the intermediate pore size zeolites such as ZSM-5. Non-zeolitic molecular sieves such as MeAPO-5, MeAPSO-5, as well as the mesoporous crystalline materials such as MCM-41 may be used as the sieve component of the catalyst. Metals such as vanadium, zinc, iron, cobalt, and gallium were found to be effective for the reduction of sulfur in the gasoline, with vanadium being the preferred metal. The amount of the metal component in the sulfur reduction additive catalyst is normally from 0.2 to 5 weight percent, but amounts up to 10 weight percent were stated to give some sulfur removal effect. The sulfur reduction component may be a separate particle additive or part of an integrated cracking/sulfur reduction catalyst. When used as a separate particle additive catalyst, these materials are used in combination with an active catalytic cracking catalyst (normally a faujasite such as zeolite Y and REY, especially as zeolite USY and REUSY) to process hydrocarbon feedstocks in the FCC unit to produce low-sulfur products.

In application Ser. Nos. 09/221,539 and 09/221,540, both filed Dec. 28, 1998, sulfur reduction catalyst similar to the one described in application Ser. No. 09/144,607 were described, however, the catalyst compositions in those applications also comprise at least one rare earth metal component (e.g. lanthanum) and a cerium component, respectively. The amount of the metal component in the sulfur reduction catalysts is normally from 0.2 to 5 weight percent, but amounts up to 10 weight percent were suggested to give some sulfur removal effect.

In application Ser. No. 09/399,637, filed Sep. 20, 1999, an improved catalytic cracking process for reducing the sulfur content of the liquid cracking products, especially cracked gasoline, produced from hydrocarbon feed containing organosulfur compounds is described. The process employs a catalyst system having a sulfur reduction component containing porous catalyst and a metal component in an oxidation state greater than zero. The sulfur reduction activity of the catalyst system is increased by increasing average oxidation state of the metal component by an oxidation step following conventional catalyst regeneration. The catalyst is normally a molecular sieve such as zeolite Y, REY, USY, RESUY, Beta or ZSM-5. Non-zeolitic molecular sieves such as MeAPO-5, MeAPSO-5, as well as the mesoporous crystalline materials such as MCM-41 and MCM-48 may also be used as the sieve component of the catalyst. Amorphous and paracrystalline materials such as amorphous refractory inorganic oxides of Group 2, 4, 13 and 14 of the periodic table, for example, Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 , MgO and mixtures thereof, and paracrystalline materials such as transitional aluminas, are also contemplated as useful support components for the metal component of the sulfur reduction catalysts. The metal component is normally a metal of Groups 5, 7, 8, 9, 12 or 13 of the Periodic Table, preferably vanadium or zinc. The amount of metal in the sulfur reduction component is normally from 0.1 to 10 weight percent (as metal, relative to the weight of the support component), however, amounts up to 10 weight percent were stated to have some sulfur removal effect. The sulfur reduction component may be a separate particle additive or part of an integrated cracking/sulfur reduction catalyst. A system for increasing the oxidation state of the metal component of a gasoline sulfur reduction additive is also described.

There continues to exist a need for effective ways to further reduce the sulfur content of gasoline and other liquid cracking products. The present invention was developed in response to this need.

SUMMARY OF THE INVENTION

The present invention is directed to sulfur reduction additive materials for use in a catalytic cracking process which materials are capable of improving the reduction in the sulfur content of liquid products produced by the cracking process, in particular, the gasoline and middle distillate cracking fractions. The present sulfur reduction additives are similar to additives described in application Ser. Nos. 09/144,607, 09/221,539 and 09/221,540, in that the additive materials employ a sulfur reduction component containing a metal component in an oxidation state greater than zero, i.e. vanadium. The sulfur reduction component in application Ser. Nos. 09/144,607, 09/221,539 and 09/221,540 comprises a molecular sieve (preferably, a zeolitic molecular sieve) which contains a metal component in an oxidation state above zero, i.e. vanadium, within the interior of the pore structure. In contrast, the sulfur reduction additives of the present invention, comprise a non-molecular sieve support

material which contains a relatively high content of vanadium metal. It has been found that the use of a non-molecular sieve catalyst support in combination with a relatively high concentration of vanadium enhances the rate of transport of vanadium over the entire FCC catalyst inventory, thereby increasing the activity of the catalyst to remove sulfur.

According to the present invention, the sulfur reduction additives comprise a non-molecular sieve catalyst support material containing a high content of vanadium in an oxidation state greater than zero. The support material may be organic or inorganic in nature and may be porous or non-porous. Preferably, the support material is an amorphous or paracrystalline inorganic oxide such as, for example, Al_2O_3 , SiO_2 , clays or mixtures thereof. The sulfur reduction additives are used as a separate particle additive in combination with the conventional catalytic cracking catalyst (normally a faujasite such as zeolite Y) to process hydrocarbon feedstocks in the fluid catalytic cracking (FCC) unit to produce low-sulfur gasoline and other liquid cracking products, such as, for example, light cycle oil that can be used as a low sulfur diesel blend component or as heating oil.

Accordingly, it is an advantage of the present invention to provide sulfur reduction additive compositions which provide improved liquid product sulfur reduction when compared to the sulfur reduction activity of a base FCC catalyst conventionally used in the catalyst cracking process.

It is also an advantage of the present invention to provide high vanadium containing sulfur reduction additive compositions which allow for the rapid dispersion of vanadium over the entire cracking catalyst inventory used in a catalytic cracking process, thereby enhancing the removal of sulfur components from cracked hydrocarbon products.

An additional advantage of the present invention is to provide sulfur reduction additive compositions having improved product sulfur reduction at lower additive levels than heretofore used for conventional sulfur reduction additives, including vanadium/zeolite sulfur reduction additives disclosed in related application Ser. Nos. 09/144,607, 09/221,539 and 09/221,540.

DETAIL DESCRIPTION OF THE INVENTION

For purposes of this invention the term "high vanadium content" or "high content of vanadium" is used herein to indicate a vanadium content of greater than 1.5 weight percent (as metal, relative to the total weight of the additive material).

The term "molecular sieve" is used herein to designate a class of polycrystalline materials that exhibits selective sorption properties which separates components of a mixture on the basis of molecular size and shape differences, and have pores of uniform size, i.e., from about 3 Å to approximately 100 Å, which pore sizes are uniquely determined by the unit structure of the crystals. Materials such as activated carbons, activated alumina and silica gels are specifically excluded since they do not possess an ordered crystalline structure and consequently have pores of a non-uniform size. The distribution of the pore diameters of such material may be narrow (generally from about 20 Å to about 50 Å) or wide (ranging from about 20 Å to several thousand Å) as in the case for some activated carbons. See R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, pp. 1-4 and D. W. Breck, *Zeolite Molecular Sieves*, pp. 1-30. A molecular sieve framework is based on an extensive three-dimensional network of oxygen atoms containing generally tetrahedral type-sites. In addition to the Si^{+4} and Al^{+3}

that compositionally define a zeolite molecular sieves, other cations also can occupy these sites. These need not be iso-electronic with Si^{+4} or Al^{+3} , but must have the ability to occupy framework sites. Cations presently known to occupy these sites within molecular sieve structures include but are not limited to Be, Mg, Zn, Co, Fe, Mn, Al, B, Ga, Fe, Cr, Si, Ge, Mn, Ti, and P. Another class of materials intended to fall within the scope of molecular sieve includes mesoporous crystalline materials exemplified by the MCM-41 and MCM-48 materials. These mesoporous crystalline materials are described in U.S. Pat. Nos. 5,098,684; 5,102,643; and 5,198,203.

In accordance with the present invention, the sulfur content of the gasoline portion of the liquid cracking products, is effectively brought to lower and more acceptable levels by carrying out the catalytic cracking in the presence of the sulfur reduction additives comprising a high content of vanadium incorporated into a non-molecular sieve catalyst support material. While the mechanism by which the high vanadium-containing additives act to enhance removal of sulfur components normally present in cracked hydrocarbon products is not precisely understood, it is believed that the additive acts to rapidly transport vanadium over the entire cracking catalyst inventory. Such an increased dispersion of vanadium permits a more efficient rate of removal of liquid product sulfur than obtainable when using a base or conventional cracking catalyst alone or in combination with conventional sulfur reduction additives heretofore used in catalyst cracking processes.

FCC Process

The present sulfur removal additives are used as a component of the circulating inventory of catalyst in the catalytic cracking process, which these days is almost invariably the FCC process. For convenience, the invention will be described with reference to the FCC process although the present additives could be used in the older moving bed type (TCC) cracking process with appropriate adjustments in particle size to suit the requirements of the process. Apart from the addition of the present additive to the catalyst inventory and some possible changes in the product recovery section, discussed below, the manner of operating the process will remain unchanged. Thus, conventional FCC catalysts may be used, for example, zeolite based catalysts with a faujasite cracking component as described in the seminal review by Venuto and Habib, *Fluid Catalytic Cracking with Zeolite Catalysts*, Marcel Dekker, New York 1979, ISBN 0-8247-6870-1 as well as in numerous other sources such as Sadeghbeigi, *Fluid Catalytic Cracking Handbook*, Gulf Publ. Co. Houston, 1995, ISBN 0-88415-290-1.

Somewhat briefly, the fluid catalytic cracking process in which the heavy hydrocarbon feed containing the organo-sulfur compounds will be cracked to lighter products takes place by contact of the feed in a cyclic catalyst recirculation cracking process with a circulating fluidizable catalytic cracking catalyst inventory consisting of particles having a size ranging from about 20 to about 100 microns. The significant steps in the cyclic process are:

- (i) the feed is catalytically cracked in a catalytic cracking zone, normally a riser cracking zone, operating at catalytic cracking conditions by contacting feed with a source of hot, regenerated cracking catalyst to produce an effluent comprising cracked products and spent catalyst containing coke and strippable hydrocarbons;
- (ii) the effluent is discharged and separated, normally in one or more cyclones, into a vapor phase rich in cracked product and a solids rich phase comprising the spent catalyst;

(iii) the vapor phase is removed as product and fractionated in the FCC main column and its associated side columns to form liquid cracking products including gasoline;

(iv) the spent catalyst is stripped, usually with steam, to remove occluded hydrocarbons from the catalyst, after which the stripped catalyst is oxidatively regenerated to produce hot, regenerated catalyst which is then recycled to the cracking zone for cracking further quantities of feed.

The present sulfur reduction additives are used in the form of a separate particle additive which is added to the main cracking catalyst in the FCCU. The cracking catalyst will normally be based on a faujasite zeolite active cracking component, which is conventionally zeolite Y in one of its forms such as calcined rare-earth exchanged type Y zeolite (CREY), the preparation of which is disclosed in U.S. Pat. No. 3,402,996, ultrastable type Y zeolite (USY) as disclosed in U.S. Pat. No. 3,293,192, as well as various partially exchanged type Y zeolites as disclosed in U.S. Pat. Nos. 3,607,043 and 3,676,368. The active cracking component is routinely combined with a matrix material such as alumina in order to provide the desired mechanical characteristics (attrition resistance etc.) as well as activity control for the very active zeolite component or components. The particle size of the cracking catalyst is typically in the range of 10 to 120 microns for effective fluidization. As a separate particle additive, the sulfur reduction additive is normally selected to have a particle size comparable with that of the cracking catalyst so as to prevent component separation during the cracking cycle. In general the particle size of the sulfur reduction additive is in the range of about 10 to about 200 microns, preferably, about 20 to about 120 microns.

Sulfur Reduction Component

According to the present invention, the sulfur reduction additives comprise on-molecular sieve support materials having a high content of vanadium. In one embodiment of the invention, the support materials are amorphous and paracrystalline support materials, such as refractory inorganic oxides of Groups 4, 13 and 14 of the Periodic Table. Suitable refractory inorganic oxides include, but are not limited to, Al_2O_3 , SiO_2 , TiO_2 , clay (e.g. kaolin, bentonite, hectorite, montmorillonite and the like) and mixtures thereof. Preferably, the support materials are selected from the group consisting of Al_2O_3 , SiO_2 , clay (preferably kaolin) and mixtures thereof. Most preferably, the support material is alumina.

In another embodiment of the invention, the support material is an activated carbon. Support materials in accordance with the invention may be used alone or in combination to prepare sulfur reduction additives in accordance with the invention.

The amount of vanadium metal contained in sulfur reduction additives in accordance with the invention catalyst is normally from about 2.0 to about 20 weight percent, typically from about 3 to about 10 weight percent, most preferably from about 5 to about 7 weight percent (metal, based on the total weight of the additive). Vanadium may be added to the support in any suitable manner sufficient to adsorb and/or absorb a suitable vanadium containing compound onto or into the support material.

In one embodiment, the sulfur reduction additives are prepared by treating the support material with an aqueous or non-aqueous solution of a suitable vanadium compound to impregnate the vanadium compound into or onto the surface of the support material. Alternatively, vanadium may be added to the support by spray drying an aqueous slurry

containing the support material and the desired vanadium compound. Non-limiting example of suitable vanadium compounds useful to prepare additives in accordance with the invention include, but are not limited to, vanadium oxalate, vanadium sulfate, organometallic vanadium complexes (e.g. vanadyl naphthenate), vanadium halides and oxyhalides (e.g. vanadium chlorides and oxychlorides) and mixtures thereof.

Following addition of the vanadium component, the support material is dried and calcined, typically at temperatures ranging from about 100 to about 800° C.

Sulfur Reduction Catalyst Use

The sulfur reduction additives of the invention are used as separate particle additives to permit optimization of the transport of vanadium to the cracking catalyst inventory. Generally, the additives of the invention are used in an amount sufficient to increase the amount of vanadium on the cracking catalyst by about 100 to about 10,000 ppm, preferably about 500 to about 5000 ppm, most preferably about 1000 to about 2000 ppm, relative to the amount of vanadium initially present on the cracking catalyst. As will be understood by one skilled in the art, the amount of vanadium transported from the additive to the catalyst is readily determined by separating the additive from the cracking catalyst by skeletal density differences and analyzing each fraction for vanadium content after subjection to catalytic cracking condition in the presence of the additive.

The sulfur reduction additive is typically used in an amount from about 0.1 to about 10 weight percent of the cracking catalyst inventory in the FCCU; preferably, the amount will be from about 0.5 to about 5 weight percent. About 2 weight percent represents a norm for most practical purposes. The additive may be added in the conventional manner, with make-up catalyst to the regenerator or by any other convenient method. The additive remains active for sulfur removal for extended periods of time although very high sulfur feeds may result in loss of sulfur removal activity in shorter times.

Other catalytically active components may be present in the circulating inventory of catalytic material in addition to the cracking catalyst and the sulfur removal additive. Examples of such other materials include the octane enhancing catalysts based on zeolite ZSM-5, CO combustion promoters based on a supported noble metal such as platinum, stack gas desulfurization additives such as DESOX™ (magnesium aluminum spinel), vanadium traps and bottom cracking additives, such as those described in Krishna, Sadeghbeigi, op cit and Scherzer, *Octane Enhancing Zeolitic FCC Catalysts*, Marcel Dekker, New York, 1990, ISBN 0-8247-8399-9. These other components may be used in their conventional amounts.

The effect of the present additives is to reduce the sulfur content of liquid cracking products, especially the light and heavy gasoline fractions, although reductions are also noted in the light cycle oil, making them more suitable for use as a diesel or home heating oil blend component. The sulfur removed by the use of the FCC catalyst is converted to the inorganic form and released as hydrogen sulfide which can be recovered in the normal way in the product recovery section of the FCCU in the same way as the hydrogen sulfide conventionally released in the cracking process. The increased load of hydrogen sulfide may impose additional sour gas/water treatment requirements but with the significant reductions in gasoline sulfur achieved, these are not likely to be considered limitative.

Very significant reductions in gasoline sulfur can be achieved by the use of the present catalysts, in some cases

up to about 80% relative to the base case using a conventional cracking catalyst, at constant conversion, using the preferred form of the catalyst described above. Gasoline sulfur reduction of 10 to 60% is readily achievable with additives according to the invention, as shown by the Examples below. The extent of sulfur reduction may depend on the original organic sulfur content of the cracking feed, with the greatest reductions achieved with the higher sulfur feeds. Sulfur reduction may be effective not only to improve product quality but also to increase product yield in cases where the refinery cracked gasoline end point has been limited by the sulfur content of the heavy gasoline fraction; by providing an effective and economical way to reduce the sulfur content of the heavy gasoline fraction, the gasoline end point may be extended without the need to resort to expensive hydrotreating, with a consequent favorable effect on refinery economics. Removal of the various thiophene derivatives which are refractory to removal by hydrotreating under less severe conditions is also desirable if subsequent hydrotreatment is contemplated.

In order to further illustrate the present invention and the advantages thereof, the following specific examples are given. The examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. All part and percentages in the examples as well as the remainder of the specification are by weight unless otherwise specified.

The scope of the invention is not in any way intended to be limited by the examples set forth below. The examples include the preparation of sulfur reduction additives in accordance with the invention and evaluations of the performance of the additives to reduce sulfur in a catalytic cracking environment.

EXAMPLES

Example 1

Preparation of 2% Vanadium and 5% Vanadium on an Al₂O₃ Support

A spray dried Al₂O₃ particle was prepared by peptizing a pseudoboehmite Al₂O₃ slurry with HCl, milling it with a Drais mill and then spray drying the milled slurry. The resulting spray dried alumina was calcined for 1 hour at 800° C.

The spray dried, calcined Al₂O₃ was then impregnated to incipient wetness with an aqueous vanadium oxalate solution. The concentration of vanadium oxalate in the solution was adjusted to produce a concentration of 2 wt % V and 5 wt % V on alumina.

The impregnated alumina was dried at 100° C. and then calcined for 2 hours at 540° C.

Example 2

Preparation of 6% V on an Al₂O₃ Support

A spray dried, calcined Al₂O₃, prepared as described in Example 1 above, was impregnated to incipient wetness with an aqueous vanadium sulfate solution. The concentration of vanadium sulfate in solution was adjusted to produce 6 wt % V on alumina.

The impregnated material was dried at 120° C. The final material was analyzed by ICP and found to contain 5.4 wt % V, 0.1 wt % Na₂O, 11% SO₄. The surface area, as determined by N₂-BET, was 39 m²/g.

Example 3

Preparation of 2.0% V on a SiO₂-Clay Support

A silica hydrogel (280–350 m²/g, 30–35% solids and 8.0–8.5 pH) was slurried in distilled water and sand milled to give a slurry which contained 14.8 wt % solids. A mixture of 13,514 g of the milled silica hydrogel slurry, 2500 g of Nalco Grade 1140 colloidal SiO₂ and 2353 g of Natka clay were Draiss milled and spray dried. The spray-dried samples were then calcined for 40 minutes at 700° C.

300 g of the calcined, spray dried sample was impregnated with an aqueous solution of vanadium sulfate to give 2 wt % V. After impregnation the sample was dried at 120° C. The final material was analyzed by ICP and found to contain 2.0 wt % V, 0.39 wt % Na₂O, 4.2% SO₄. The surface area, as determined by N₂-BET, was 115 m²/g.

Example 4

Preparation of 0.42% Vanadium/Zelite Additive

A vanadium/zeolite catalyst was prepared by spray-drying a slurry of 50% USY, 30% clay and 20% silica sol. The spray-dried material was ammonium exchanged to remove the Na⁺, rare earth exchanged and then dried at 100° C. Vanadium was added by impregnation of the catalyst to incipient wetness using an aqueous vanadium oxalate solution. The amount of vanadium oxalate in solution was adjusted to a target of 0.4 wt %.

The final material was analyzed by ICP and found to contain 0.42 wt % V, 3.8 wt % RE₂O₃ and 0.27 wt % Na₂O. The surface area as determined by N₂-BET, was 375 m²/g.

Example 5

Catalytic Evaluation of Vanadium Supported on Al₂O₃

The V/Al₂O₃ additives from Example 1 were blended with a commercial FCC catalyst and steam deactivated in a fluidized bed for 4 hours at 1500° F. in 100% steam. The additive/FCC catalyst blends were designed so that the blend contained 1000 ppm V (95 wt % FCC Catalyst/5 wt % of 2% V/Al₂O₃ additive; and 98 wt % FCC Catalyst/2 wt % of 5% V/Al₂O₃ additive).

The additive/FCC catalyst blends were tested for gas oil cracking activity and selectivity using an ASTM Microactivity Test ("MAT") (ASTM procedure D-3907). The liquid product from each run was analyzed for sulfur using a gas chromatograph with an Atomic Emission Detector (GC-AED). Analysis of the liquid products with the GC-AED allows each of the sulfur species in the gasoline region to be quantified. For purposes of this example, the cut gasoline will be defined as C₃ to C₁₂ hydrocarbons that have a boiling point up to 430° F. The sulfur species included in the cut of gasoline range include thiophene, tetrahydrothiophene, C₁–C₅ alkylated thiophenes and a variety of aliphatic sulfur species. Benzothiophene is not included in the cut gasoline range. The properties of the gas oil feed used in the MAT test are shown in the Table 1.

TABLE 1

Properties of Vacuum Gas Oil Feed	
API Gravity	26.6
Aniline Point, ° F.	182

TABLE 1-continued

Properties of Vacuum Gas Oil Feed	
CCR, wt %	0.23
Sulfur, wt %	1.05
Nitrogen, ppm	600
Basic Nitrogen, ppm	310
Ni, ppm	0.32
V, ppm	0.68
Fe, ppm	9.15
Cu, ppm	0.05
Na, ppm	2.93
Distillation	
IBP, ° F.	358
50 wt %, ° F.	716
99.5 wt %, ° F.	1130

The MAT data for the catalysts is shown in the Table 2; where the product selectivity was interpolated to a constant conversion of 70 wt %. The first column shows the FCC catalyst without the vanadium-based sulfur reduction additive. The next two columns show FCC catalyst blended with the 2 wt % V and 5 wt % V additives, respectively. The data shows that both vanadium additives decrease cut gasoline range sulfur 55–65% as compared to the base FCC catalyst. The coke and H₂ increase modestly for the samples that contain the vanadium additives.

TABLE 2

MAT Product catalyst Yields	Base FCC Catalyst	95 wt % FCC Catalyst	98 wt % FCC Catalyst
		5 wt % (2% V/Al ₂ O ₃)	2 wt % (5% V/Al ₂ O ₃)
Conversion	70	70	70
Cat/Oil	2.8	3.5	3.6
H ₂ Yields, wt %	0.06	0.20	0.22
C1 + C2 Gas, wt %	1.40	1.55	1.58
Total C3 Gas, wt %	4.97	4.97	5.02
Propylene, wt %	4.06	4.06	4.10
Total C4 Gas, wt %	9.96	10.02	9.94
C5 + gasoline, wt %	51.07	49.83	50.17
LCO, wt %	25.77	25.85	25.90
Bottoms, wt %	4.13	4.10	4.20
Coke, wt %	2.55	3.11	3.18
Cut Gasoline	263	112	98
S, ppm			
% Reduction in Cut Gasoline Sulfur	Base	57%	63%

Example 6

Catalytic Evaluation of V/Al₂O₃ Steamed Deactivated Together and Separately from the FCC Catalyst

The need for transport of vanadium from the additive to the catalyst during deactivation in order to achieve good cut gasoline sulfur reduction is demonstrated in this example. The 6% V/Al₂O₃ additive from Example 2 was blended at a 4 wt % level with a FCC equilibrium catalyst (120 ppm V and 60 ppm Ni) and mildly steam deactivated for 20 hours at 1350° F. in 25% steam to simulate catalytic cracking conditions.

Separation of the additive from Ecat by skeletal density differences and analysis of the fractions by ICP shows that on the ECAT fraction, the vanadium content has increased from 120 ppm V to 2360 ppm V during the steaming process. A comparison example was made by steam deac-

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tivating the Ecat and the 6% V/Al₂O₃, additive each separately, for 20 hours at 1350° F. in 25% steam, and then blending the additive at a 4 wt % level. The base case Ecat was also steamed for 20 hours at 1350° F. in 25% steam. The steam deactivated Ecat and the Additive/FCC catalyst blends were tested for gas oil cracking and selectivity using ASTM Microactivity Test ("MAT") (ASTM procedure D-3907) as described in Example 5. The properties of the gas oil used in this example are shown in Table 1.

The MAT data for the catalyst is shown in the Table 3, where the product selectivity was interpolated to a constant conversion of 70 wt %. The first column shows data for the FCC Ecat without the vanadium based sulfur reduction additive. The second column shows data for the FCC Ecat steamed together with the V/Al₂O₃ additive. The third column shows data for the FCC Ecat and V/Al₂O₃, additive steamed separately and then blended together. The data shows that when the additive is steamed together with the FCC catalyst (as typical of catalytic cracking process conditions) vanadium is transported from the additive to the catalyst to provide a substantial cut in gasoline sulfur reduction. The coke and H₂ increased modestly for the samples that contain the vanadium additives.

TABLE 3

MAT Product Yield	Base Equilibrium Catalyst	96 wt % FCC ECAT 4 wt % (6% V/Al ₂ O ₃) Steamed Together	96 wt % FCC ECAT 4 wt % (6% V/Al ₂ O ₃) Steamed Separately
Conversion	70	70	70
Cat/Oil	3.70	4.26	4.26
H ₂ Yields, wt %	0.04	0.09	0.10
C1 + C2 Gas, wt %	1.37	1.50	1.45
Total C3 Gas, wt %	5.07	5.29	5.15
Propylene, wt %	4.38	4.58	4.45
Total C4 Gas, wt %	10.02	10.44	10.15
C5 + gasoline, wt %	50.94	49.76	50.10
LCO, wt %	25.38	25.21	25.16
Bottoms, wt %	4.42	4.57	4.57
Coke, wt %	2.13	2.48	2.54
Cut Gasoline S, ppm	525	359	521
% Reduction in Cut Gasoline Sulfur	Base	32	1

Example 7

Catalytic Evaluation of Vanadium Supported on SiO₂/Clay

The 2% V/SiO₂/Clay additive from Example 3 was blended at a 5% level with a FCC Ecat (120 ppm V and 60 ppm Ni) and mildly steam deactivated for 20 hours at 1350° F. in 25% steam. As a comparison, the base Ecat was also deactivated under those conditions. The steam deactivated base Ecat and the additive FCC blends were tested for gas oil cracking activity and selectivity using an ASTM Microactivity Test (ASTM procedure D-3907) as described in Example 5. The properties of the gas oil used in this example are shown in Table 4.

The MAT data for the catalysts is shown in Table 5, where the product selectivity was interpolated to a constant conversion of 70 wt %. The data shows that the V/SiO₂/Clay additive decreases cut gasoline sulfur 42% as compared to the base case Ecat.

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TABLE 4

Properties of Vacuum Gas Oil Feed	
API Gravity	25.3
Aniline Point, ° F.	178
CCR, wt %	0.21
Sulfur, wt %	1.04
Nitrogen, ppm	700
Basic Nitrogen, ppm	308
Ni, ppm	0.2
V, ppm	0.4
Fe, ppm	3.7
Cu, ppm	0
Na, ppm	0
Distillation	
IBP, ° F.	309
50 wt %, ° F.	748
99.5 wt %, ° F.	1063

TABLE 5

MAT Product Yields	Base Ecat	95% Ecat 5%{2% V/SiO ₂ /Clay}
Conversion	70	70
Cat/Oil	3.64	4.05
H ₂ Yield	0.05	0.10
C1 + C2 Gas	1.33	1.39
Total C3 Gas, wt %	4.53	4.58
Total C4 Gas, wt %	9.69	9.39
C5 + gasoline, wt %	51.86	51.56
LCO, wt %	24.61	23.97
Bottoms, wt %	5.31	5.44
Coke, wt %	2.26	2.53
Cut Gasoline S, ppm	616	361
% Reduction in Cut Gasoline Sulfur	Base	42

Example 8

Catalytic Cracking Performance of 6% V/Alumina Versus V/Zeolite Catalyst

This example shows the utility of the high vanadium-containing additive in circulating FCC riser/regenerator

pilot plant testing. The high vanadium-containing additive described in Example 2 was tested in a Davison Circulating Riser pilot plant with a commercial FCC feed and equilibrium catalyst. For comparison, the vanadium/zeolite additive described in Example 4 was also tested. The equilibrium catalyst contained 332 ppm Ni and 530 ppm V. The feed properties are shown in Table 6. The DCR was operated with a riser temperature of 980° F. and a regenerator temperature of 1300° F. All the liquid products were analyzed by GC-AED for gasoline sulfur levels.

The testing results are shown in Table 7. The high vanadium-containing additive tested at a 2 wt % additive level gave 33% cut gasoline sulfur reduction as compared to the base Ecat. The vanadium/zeolite additive decreased cut gasoline sulfur 13% when used at the 22% additive level and 26% when used at the 50% additive level. The coke and hydrogen yields were marginally higher for the high vanadium-containing additive than for the base case Ecat.

TABLE 6

Properties of Vacuum Gas Oil Feed	
API Gravity	23.9
Aniline Point, ° F.	186
CCR, wt %	0.62
Sulfur, wt %	1.50
Nitrogen, ppm	1000
Basic Nitrogen, ppm	140
Ni, ppm	0.3
V, ppm	0.3
Fe, ppm	0.7
Cu, ppm	0
Na, ppm	0.9
Distillation	
IBP, ° F.	429
50 wt %, ° F.	783
99.5 wt %, ° F.	1292

TABLE 7

DCR Product Yields	Base FCC Catalyst	78 wt % FCC Cat. 22% V/Zelite Cat.	50 wt % FCC Cat. 50% V/Zelite Cat.	98 wt % FCC Cat. 2% (6% V/Al ₂ O ₃)
Conversion	72	72	72	72
Cat/Oil	6.69	6.47	6.61	7.92
H ₂ Yield	0.03	0.04	0.05	0.08
C1 + C2 Gas	2.41	2.53	2.63	2.37
Total C3 Gas, wt %	6.68	6.59	6.66	6.29
Total C4 Gas, wt %	12.41	12.06	12.24	11.79
C5 + gasoline, wt %	45.95	46.11	45.51	46.20
LCO, wt %	20.59	20.28	20.15	20.66
Bottoms, wt %	7.41	7.72	7.85	7.34
Coke, wt %	4.11	4.02	4.24	4.58
Cut Gasoline S, ppm	877	765	651	589
% Reduction in Cut Gasoline Sulfur	Base case	13	26	33

Reasonable variations and modifications, which will be apparent to those skilled in the art, can be made in this invention without departing from the spirit and scope thereof.

We claim:

1. A method of reducing the sulfur content of a liquid catalytically cracked petroleum fraction, which comprises catalytically cracking a petroleum feed fraction containing organosulfur compounds at elevated temperature in the presence of an equilibrium cracking catalyst and a product sulfur reduction additive to produce liquid cracking products of reduced sulfur content, wherein the product sulfur addi-

tive consists essentially of vanadium and a support selected from the group consisting of a refractory inorganic oxide and activated carbon.

2. A method according to claim 1 wherein said support comprises a refractory inorganic oxide selected from the group consisting of alumina, silica, titania, clay and mixtures thereof.

3. A method according to claim 1 in which the equilibrium cracking catalyst comprises a large pore size zeolite.

4. A method according to claim 3 in which the large pore size zeolite comprises a faujasite.

5. A method according to claim 2 in which the refractory inorganic oxide is selected from the group consisting of alumina, silica, clay and mixtures thereof.

6. A method according to claim 5 in which the refractory inorganic oxide is alumina.

7. A method according to claim 1 in which the product sulfur reduction additive contains from about 2 to about 20 weight percent, based on the total weight of the additive, of vanadium.

8. A method according to claim 7 in which the product sulfur reduction additive contains from about 5 to about 10 weight percent, based on the total weight of the additive, of vanadium.

9. A method according to claim 1 in which vanadium has been impregnated onto the surface of the support.

10. A method according to claim 1 in which vanadium has been incorporated into the support.

11. A method according to claim 1 in which the sulfur reduction additive is a separate particle.

12. In a fluid catalytic cracking process in which a heavy hydrocarbon feed comprising organosulfur compounds is catalytically cracked to lighter products by contact in a cyclic catalyst cracking process with a circulating equilibrium cracking catalyst inventory consisting of particles having a size ranging from about 20 to about 100 microns, comprising:

(i) catalytically cracking the feed in a catalytic cracking zone operating at catalytic cracking conditions by con-

tacting feed with a source of regenerated equilibrium cracking catalyst to produce a cracking zone effluent comprising cracked products and spent catalyst containing coke and strippable hydrocarbons;

(ii) discharging and separating the effluent mixture into a cracked product rich vapor phase and a solids rich phase comprising spent catalyst;

(iii) removing the vapor phase as a product and fractionating the vapor to form liquid cracking products including gasoline,

(iv) stripping the solids rich spent catalyst phase to remove occluded hydrocarbons from the catalyst,

15

- (v) transporting stripped catalyst from the stripper to a catalyst regenerator;
- (vi) regenerating stripped catalyst by contact with oxygen containing gas to produce regenerated catalyst; and
- (vii) recycling the regenerated catalyst to the cracking zone to contact further quantities of heavy hydrocarbon feed, the improvement which comprises

reducing the sulfur content of a the gasoline portion of the liquid cracking products, by catalytically cracking the feed fraction at elevated temperature in the presence of the equilibrium catalyst and a product sulfur reduction additive to produce liquid cracking products of reduced sulfur content, wherein the product sulfur additive comprises fluidizable particles having a size ranging from about 20 to about 100 microns and consists essentially of vanadium and a support selected from the group consisting of a refractory inorganic oxide and activated carbon.

13. A method according to claim 12 in which the support comprises a refractory inorganic oxide selected from the group consisting of alumina, silica, titania, clay and mixtures thereof.

14. A method according to claim 12 in which the equilibrium cracking catalyst comprises a matrixed faujasite zeolite.

15. A method according to claim 13 in which the support is a refractory inorganic oxide support selected from the group consisting of alumina, silica, clay and mixtures thereof.

16. A method according to claim 15 in which the refractory inorganic oxide is alumina.

17. A method according to claim 12 in which the product sulfur reduction additive contains from about 2 to about 20 weight percent, based on the total weight of the additive, of vanadium metal.

18. A method according to claim 17 in which the product sulfur reduction additive contains from about 5 to about 10 weight percent, based on the total weight of the additive, of vanadium metal.

16

19. A method according to claim 12 in which vanadium has been impregnated onto or into the surface of the support.

20. A method according to claim 12 in which vanadium has been added into the support.

21. A method according to claim 12 in which the sulfur reduction additive is a separate particle.

22. A method according to claim 12 in which the gasoline product of reduced sulfur content is a gasoline boiling range fraction which has a sulfur content lower than that achieved in the absence of the product sulfur reduction additive.

23. A method of reducing the sulfur content of a catalytically cracked liquid product petroleum fraction, which comprises catalytically cracking a petroleum feed fraction containing organosulfur compounds at elevated temperature in the presence of an equilibrium cracking catalyst containing vanadium in intimate contact with separate particles of at least one product sulfur reduction additive to produce liquid cracking products of reduced sulfur content, wherein the additive consists essentially of a support selected from the group consisting of a refractory inorganic oxide and activated carbon, and at least one transportable vanadium compound adsorbed and/or absorbed onto or into the support, respectively, and capable of being transported to the cracking catalyst in amounts sufficient to increase the vanadium content of the equilibrium cracking catalyst by about 100 ppm to about 10,000 ppm, relative to the amount of vanadium initially present on the equilibrium cracking catalyst, when the additive is contacted with the equilibrium cracking catalyst under catalytic cracking conditions.

24. The method of claim 23 wherein the support comprises a refractory inorganic oxide selected from the group consisting of alumina, silica, titania, clay and mixtures thereof.

25. The method of claim 23 wherein the vanadium content of the equilibrium cracking catalyst is increased by about 500 to about 5000 ppm.

26. The method of claim 23 wherein the vanadium content of the equilibrium cracking catalyst is increased by about 1000 to about 2000 ppm.

* * * * *

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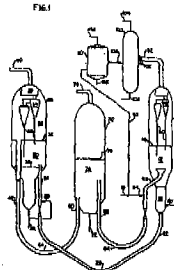
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(21) Method of reducing coke formation in heavy hydrocarbon feed catalytic cracking.

(22) A method for decreasing the amount of coke produced during the cracking of hydrocarbon feedstock to lower molecular weight products in a reaction zone (10), where the feedstock contains at least two metal contaminants selected from nickel, vanadium and iron, and where these contaminants become deposited on the catalyst, comprises passing the catalyst through a reduction zone (70) maintained at an elevated temperature for a time sufficient to at least partially passivate the catalyst before the catalyst enters the reaction zone (10). The amount of coke may be decreased still further by the addition to reaction zone (10) of a hydrogen donor material which may be, e.g., a hydrogenated fraction (82) of the cracked product (52).

FIG. 1



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1 zone operated for incomplete combustion of the coke
2 to CO₂ by periodically increasing the oxygen con-
3 centration above that required for complete combus-
4 tion of the coke and by maintaining the temperature
5 above 1300°F. This patent does not disclose a
6 method for passivating metals-contaminated catalyst
7 in a system where the regeneration zone is routinely
8 operated for complete combustion of the coke.

9 U.S. Patent No. 4,162,213 is directed at
10 decreasing the catalytic activity of metal contamin-
11 ants present in cracking catalyst by regenerating the
12 catalyst at temperatures of 1300-1400°F in such a
13 manner as to leave less than 0.10 wt. % residual
14 carbon on the catalyst.

15 Cimbalò, Foster and Wachtel in an article
16 entitled "Deposited Metals Poison FCC Catalyst"
17 published at pp 112-122 of the May 15, 1972 issue of
18 Oil and Gas Journal disclose that the catalytic
19 activity of metal contaminants decrease with repeated
20 oxidation and reduction cycles.

21 U.S. Patent No. 3,718,553 is directed at
22 the use of a cracking catalyst impregnated with
23 100-1000 parts per million by weight (WPPM) of iron,
24 nickel or vanadium or a combination of these metals
25 to increase the octane number of the cracked hydro-
26 carbon products. This reference does not recognize
27 that use of certain of these metals may adversely
28 affect the catalyst selectivity or activity.

29 U.S. Patent Nos. 3,479,279 and 4,035,285
30 disclose hydrotreating of catalytic cracker product
31 cuts and recirculating this product to the catalytic
32 cracker. Related U.S. Patent Nos. 3,413,212 and
33 3,533,936 disclose the use of hydrogen donor mate-
34 rials for decreasing the rate of coke formation on
35 cracking catalyst. These patents each disclose in

1 BACKGROUND OF THE INVENTION

2 This invention relates to a method for
3 decreasing the catalytic activity of metal contam-
4 inants on cracking catalysts and for decreasing the
5 hydrogen and coke formation on cracking catalysts.
6 More specifically, this invention is directed to a
7 method for reducing the coke and hydrogen formation
8 caused by metal contaminants, such as nickel, vana-
9 dium and/or iron, which have become deposited upon
10 cracking catalysts from feedstock containing same.

11 In the catalytic cracking of hydrocarbon
12 feedstocks, particularly heavy feedstocks, vanadium,
13 nickel and/or iron present in the feedstock becomes
14 deposited on the cracking catalyst promoting exces-
15 sive hydrogen and coke makes. These metal contamin-
16 ants are not removed during conventional catalyst
17 regeneration operations during which coke deposits on
18 the catalyst are converted to CO and CO₂. As used
19 hereinafter the term "passivation" is defined as a
20 method for decreasing the detrimental catalytic
21 effects of metal contaminants such as nickel, vana-
22 dium and iron which become deposited on catalyst.

23 U.S. Patent Nos. 3,711,422; 4,025,545;
24 4,031,002; 4,111,845; 4,141,858; 4,148,712; 4,148,714
25 and 4,166,806 all are directed to the contacting of
26 the cracking catalyst with antimony compounds to
27 passivate the catalytic activity of the iron, nickel
28 and vanadium contaminants deposited on the catalyst.
29 However, antimony compounds, alone, may not passivate
30 the metal contaminants to sufficiently low levels
31 particularly where the metal contaminant concentra-
32 tion on the catalyst is relatively high. U.S.
33 Patent No. 4,176,084 is directed to the passivation
34 of metals contaminated catalyst in a regeneration

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1 Table V that hydrotreating a fraction from a cata-
2 lytic cracking zone and returning the hydrotreated
3 material with the cat cracker feed decreases the coke
4 make in the catalytic cracking zone. These patents
5 also disclose that the hydrotreated material prefer-
6 ably is a hydrogen donor material which releases
7 hydrogen to unsaturated olefinic hydrocarbons in a
8 cracking zone without dehydrogenative action. Suit-
9 able materials disclosed are hydroaromatic, naphthene
10 aromatic and naphthenic compounds. Preferred mate-
11 rials are compounds having at least one and prefer-
12 ably 2, 3 or 4 aromatic nuclei, partially hydro-
13 genated and containing olefinic bonds. The hydrogen
14 donor material was hydrogenated by contacting the
15 donor material with hydrogen over a suitable hydro-
16 genation catalyst at hydrogenation conditions.
17 The subject invention is directed at the
18 addition of hydrogen donor material to a catalytic
19 cracking zone in which the metals contaminated
20 cracking catalyst has been passivated by passing the
21 catalyst through a reduction zone maintained at
22 an elevated temperature. The addition of hydrogen
23 donor material and passivation of the cracking
24 catalyst operate to decrease the coke makes on the
25 cracking catalyst.

26 SUMMARY OF THE INVENTION

27 This invention is directed at a method for
28 reducing the rate of coke production from a hydro-
29 carbon feedstock cracked to lower molecular weight
30 products in a reaction zone containing cracking
31 catalyst where the feedstock contains at least two
32 metals selected from the class consisting of nickel,
33 vanadium and iron and where at least some of the
34 metal contaminants become deposited on the catalyst.
35 The method comprises passing the catalyst after

regeneration from the reaction zone through a reduction zone maintained at an elevated temperature for a time sufficient to at least partially passivate the metal contaminants on the catalyst, a reducing environment maintained in the reduction zone by the addition to the reduction zone of a material selected from the class consisting of hydrogen, carbon monoxide and mixtures thereof, said passivated catalyst thereafter passing to the reaction zone without further processing. The metal contaminants may be further passivated by the addition to the reaction zone of a hydrogen donor material which transfers hydrogen to the hydrocarbon feedstock and/or to the cracked lower molecular weight products. The metal contaminants may be passivated still further by monitoring the concentration of each metal contaminant on the catalyst and adding predetermined amounts of selected metal contaminants to the system. The catalyst may be still further passivated by the addition of known passivation agents to the system. The temperature of the reduction zone preferably is maintained above about 600°C. The hydrogen donor material added to the reaction zone preferably has a boiling point between about 200°C and about 500°C. In a preferred embodiment, the hydrogen donor material is obtained by fractionating the cracked molecular products from the reaction zone, passing the desired fraction through a hydrogenation zone and then recirculating the material to the reaction zone.

BRIEF DESCRIPTION OF THE DRAWING

The Figure is a flow diagram of a fluidized catalytic cracking unit employing the subject invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the Figure, the present invention is shown as applied to a typical fluid catalytic cracking process. Various items such as pumps, compressors, steam lines, instrumentation and other process equipment has been omitted to simplify the drawing. Reaction or cracking zone 10 is shown containing a fluidized catalyst bed 12 having a level at 14 in which a hydrocarbon feedstock is introduced into the fluidized bed through lines 16 and 94 for catalytic cracking. The hydrocarbon feedstock may comprise naphthas, light gas oils, heavy gas oils, residual fractions, reduced crude oils, cycle oils derived from any of these, as well as suitable fractions derived from shale oil kerogen, tar sands, bitumen processing, synthetic oils, coal hydrogenation, and the like. Such feedstocks may be employed singly, separately in parallel reaction zones, or in any desired combination. Typically, these feedstocks will contain metal contaminants such as nickel, vanadium and/or iron. Heavy feedstocks typically contain relatively high concentrations of vanadium and/or nickel as well as coke precursors, such as Conradson carbon materials. The determination of the amount of Conradson carbon material present may be determined by ASTM test D189-65, which is incorporated herein by reference. Hydrocarbon gas and vapors passing through fluidized bed 12 maintain the bed in a dense turbulent fluidized condition. Preferably hydrogen donor material passes through line 92 for preblending with cat cracker feedstock in line 16 prior to entering fluidized catalyst bed 12 through line 94. Alternatively the hydrogen donor material may be added directly to reaction zone 10 in close proximity

to the point where the cat cracker feedstock enters reaction zone 10. Typically, the hydrogen donor material will comprise between about 5 and about 100 wt. % of the hydrocarbon feedstock to be cracked.

In reaction zone 10, the cracking catalyst becomes spent during contact with the hydrocarbon feedstock due to the deposition of coke thereon. Thus, the terms "spent" or "coke contaminated" catalyst as used herein generally refer to catalyst which has passed through a reaction zone and which contains a sufficient quantity of coke thereon to cause activity loss, thereby requiring regeneration. Generally, the coke content of spent catalyst can vary anywhere from about 0.5 to about 5 wt. % or more. Typically, spent catalyst coke contents vary from about 0.5 to about 1.5 wt. %.

Prior to actual regeneration, the spent catalyst is usually passed from reaction zone 10 into a stripping zone 18 and contacted therein with a stripping gas, which is introduced into the lower portion of zone 18 via line 20. The stripping gas, which is usually introduced at a pressure of from about 10 to about 50 psig, serves to remove most of the volatile hydrocarbons from the spent catalyst. A preferred stripping gas is steam, although nitrogen, other inert gases or flue gas may be employed. Normally, the stripping zone is maintained at essentially the same temperature as the reaction zone, i.e. from about 450°C to about 600°C. Stripped spent catalyst from which most of the volatile hydrocarbons have been removed, is then passed from the bottom of stripping zone 18, through U-bend 22 and into a connecting vertical riser 24 which extends into the lower portion of regeneration zone 26. Air

is added to riser 24 via line 28 in an amount sufficient to reduce the density of the catalyst flowing therein, thus causing the catalyst to flow upward into regeneration zone 26 by simple hydraulic balance.

In the particular configuration shown, the regeneration zone is a separate vessel (arranged at approximately the same level as reaction zone 10) containing a dense phase catalyst bed 30 having a level indicated at 32, which is undergoing regeneration to burn-off coke deposits formed in the reaction zone during the cracking reaction, above which is a dilute catalyst phase 34. An oxygen-containing regeneration gas enters the lower portion of regeneration zone 26 via line 36 and passes up through a grid 38 and the dense phase catalyst bed 30, maintaining said bed in a turbulent fluidized condition similar to that present in reaction zone 10. Oxygen-containing regeneration gases which may be employed in the process of the present invention are those gases which contain molecular oxygen in admixture with a substantial portion of an inert diluent gas. Air is a particularly suitable regeneration gas. An additional gas which may be employed is air enriched with oxygen. Additionally, if desired, steam may be added to the dense phase bed along with the regeneration gas or separately therefrom to provide additional inert diluents and/or fluidization gas. Typically, the specific vapor velocity of the regeneration gas will be in the range of from about 0.8 to about 6.0 feet/sec., preferably from about 1.5 to about 4 feet/sec.

Regenerated catalyst from the dense phase catalyst bed 30 in the regeneration zone 26 flows downward through standpipe 42 and passes through

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1 U-bend 44, and line 80 into reduction zone 70 maintained at a temperature above 500°C preferably above about 600°C having a reducing agent such as hydrogen or carbon monoxide, entering through line 72 to maintain a reducing environment in the reduction zone to passivate the contaminants as described in more detail hereinafter. The regenerated and passivated catalyst then passes from reduction zone 70 through line 82 and U-bend 84 into the reaction zone 10 by way of transfer line 46 which joins U-bend 84 near the level of the oil injection line 16 and hydrogen donor line 92.

13 By regenerated catalyst is meant catalyst leaving the regeneration zone which has contacted an oxygen-containing gas causing at least a portion, preferably a substantial portion, of the coke present on the catalyst to be removed. More specifically, the carbon content of the regenerated catalyst can vary anywhere from about 0.01 to about 0.2 wt. %, but preferably is from about 0.01 to about 0.1 wt. %. Predetermined quantities of selected metals or conventional passivation promoters may be added to the hydrocarbon feedstock through lines 16 and/or 94, if desired, as described more fully hereinafter. The hydrocarbon feedstock for the cracking process, containing minor amounts of iron, nickel and/or vanadium contaminants is injected into line 46 through line 94 to form an oil and catalyst mixture which is passed into fluid bed 12 within reaction zone 10. The metal contaminants and the passivation promoter, if any, become deposited on the cracking catalyst. Product vapors containing entrained catalyst particles pass overhead from fluid bed 12 into a gas-solid separation means 48 wherein the entrained catalyst particles are separated therefrom

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1 recycling and a further processing (not shown).
2 The at least partially hydrogenated stream exiting zone 110, also referred to as the hydrogen donor material, is recycled to the reaction zone through line 92.

6 In regeneration zone 26, flue gases formed during regeneration of the spent catalyst pass from the dense phase catalyst bed 30 into the dilute catalyst phase 34 along with entrained catalyst particles. The catalyst particles are separated from the flue gas by a suitable gas-solid separation means 54 and returned to the dense phase catalyst bed 30 via diplegs 56. The substantially catalyst-free flue gas then passes into a plenum chamber 58 prior to discharge from the regeneration zone 26 through line 60. Where the regeneration zone is operated for substantially complete combustion of the coke, the flue gas typically will contain less than about 0.2, preferably less than 0.1 and more preferably less than 0.05 volume % carbon monoxide. The oxygen content usually will vary from about 0.4 to about 7 vol. %, preferably from about 0.8 to about 5 vol. %, more preferably from about 1 to about 3 vol. %, most preferably from about 1.0 to about 2 vol. %.

25 Reduction zone 70 may be any vessel providing suitable contacting of the catalyst with a reducing environment at elevated temperatures. The shape of reduction zone 70 is not critical. In the embodiment shown, reduction zone 70 comprises a treater vessel having a shape generally similar to that of regeneration zone 26, with the reducing environment maintained, and catalyst fluidized by, reducing agent entering through line 72 and exiting through line 78. The volume of dense phase 74 having a level at 76 is dependent on the required residence time. The

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1 and returned through diplegs 50 leading back into fluid bed 12. The product vapors are then conveyed through line 52 and condenser 102 into fractionation zone 100, wherein the product stream is separated into two or more fractions. Fractionation zone 100 may comprise any means for separating the product into fractions having different boiling ranges. Typically, zone 100 may comprise a plate or packed column of conventional design. In the embodiment shown the product is separated into an overhead stream exiting through line 104, comprising light boiling materials, i.e. compounds boiling below about 200°C, a middle cut boiling in the range of about 200 to 370°C exiting through line 106 and a bottoms stream boiling above about 370°C exiting through line 108. At least a fraction of the product in line 106, preferably a major fraction, passes into hydrogenation zone 110 maintained under hydrogenating conditions where the product contacts hydrogen entering zone 110 through line 112. A gaseous stream may pass from zone 110 through line 114 for removal of any undesired by-products. Zone 110 typically will contain a conventional hydrogenating catalyst as, for example, a molybdenum salt such as molybdenum oxide or molybdenum sulfide, and a nickel or cobalt salt, such as nickel or cobalt oxides and/or sulfides. These salts typically are deposited on a support material such as alumina and/or silica stabilized alumina. Hydrogenation catalysts which are particularly suitable are described in U.S. Patent No. 3,509,044, the disclosure of which is incorporated herein by reference. Zone 110 will be maintained at a temperature ranging between about 350 and 400°C and a pressure ranging between about 600 and 3000 psi. A vapor stream exits zone 110 for

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1 residence time of the catalyst in reduction zone 70 is not critical as long as it is sufficient to effect the passivation. The residence time will range from about 5 sec. to about 30 min., typically from about 2 to 5 minutes. The pressure in this zone is not critical and generally will be a function of the location of reduction zone 70 in the system and the pressure in the adjacent regeneration and reaction zones. In the embodiment shown, the pressure in zone 70 will be maintained in the range of about 5 to 50 psia, although the reduction zone preferably should be designed to withstand pressures of 100 psia. The temperature in reduction zone 70 should be above about 500°C preferably above 600°C, but below the temperature at which the catalyst sinters or degrades. A preferred temperature range is about 600-850°C, with the more preferred temperature range being 650-750°C. The reduction zone 70 can be located either before or after regeneration zone 26, with the preferred location being after the regeneration zone, so that the heat imparted to the catalyst by the regeneration obviates or minimizes the need for additional catalyst heating. The reducing agent utilized in the reduction zone 70 is not critical, although hydrogen and carbon monoxide are the preferred reducing agents. Other reducing agents including light hydrocarbons, such as C₃ hydrocarbons, may also be satisfactory.

29 Reduction zone 70 can be constructed of any chemically resistant material sufficiently able to withstand the relatively high temperatures involved and the high attrition conditions which are inherent in systems wherein fluidized catalyst is transported. Specifically, metals are contemplated which may or may not be lined. More specifically, ceramic liners are contemplated within any and all portions of the

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1 reduction zone together with alloy use and structural
2 designs in order to withstand the maximum contemplated
3 operating temperatures.

4 The reducing agent utilized in all but one
5 of the following tests was high purity grade hydrogen,
6 comprising 99.9% hydrogen. In the remaining test,
7 shown in Table VIII a reducing agent comprising 99.3%
8 CO was utilized. It is expected that commercial
9 grade hydrogen, commercial grade CO, and process gas
10 streams containing H₂ and/or CO can be utilized.
11 Examples include cat cracker tail gas, catalytic
12 reformer off-gas, spent hydrogen streams from cata-
13 lytic hydroprocessing, synthesis gas, and flue
14 gases. The rate of consumption of the reducing agent
15 in reducing zone 70 will, of course, be dependent on
16 the amount of reducible material entering the
17 reducing zone. In a typical fluidized catalytic
18 cracking unit it is anticipated that about 10 to 100
19 scf of hydrogen or about 10 to 100 scf of CO gas
20 would be required for each ton of catalyst passed
21 through reduction zone 70.

22 If the reducing agent entering through line
23 72 is circulated through reduction zone 70 and thence
24 into other units, a gas-solids separation means may
25 be required for use in connection with the reduction
26 zone. If the reducing agent exiting from zone 70 is
27 circulated back into the reduction zone, a gas-solids
28 separation means may not be necessary. Preferred
29 separation means for zones 10, 26 and 70 will be
30 cyclone separators, multicyclones or the like whose
31 design and construction are well known in the art.
32 In the case of cyclone separators, a single cyclone
33 may be used, but preferably, more than one cyclone
34 will be used in parallel or in series flow to effect
35 the desired degree of separation.

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1 equilibrium. The residence time of the flue gas may
2 vary from about 10 to about 60 seconds in the regen-
3 eration zone and from about 2 to about 30 seconds in
4 the dense bed phase. Preferably, the residence time
5 of the flue gas varies from about 15 to about 20
6 seconds in the dense bed.

7 The present invention may be applied
8 beneficially to any type of fluid cat cracking unit
9 without limitation as to the spatial arrangement of
10 the reaction, stripping, and regeneration zones, with
11 only the addition of reduction zone 70 and related
12 elements. In general, any commercial catalytic
13 cracking catalyst designed for high thermal stability
14 could be suitably employed in the present invention.
15 Such catalysts include those containing silica and/or
16 alumina. Catalysts containing combustion promoters
17 such as platinum can be used. Other refractory metal
18 oxides such as magnesia or zirconia may be employed
19 and are limited only by their ability to be effectively
20 regenerated under the selected conditions.
21 With particular regard to catalytic cracking, preferred
22 catalysts include the combinations of silica
23 and alumina, containing 10 to 50 wt. % alumina, and
24 particularly their admixtures with molecular sieves
25 or crystalline aluminosilicates. Suitable molecular
26 sieves include both naturally occurring and synthetic
27 aluminosilicate materials, such as faujasite, cha-
28 bazite, X-type and Y-type aluminosilicate materials
29 and ultra stable, large pore crystalline aluminosilicate
30 materials. When admixed with, for example,
31 silica-alumina to provide a petroleum cracking
32 catalyst, the molecular sieve content of the fresh
33 finished catalyst particles is suitably within
34 the range from 5-35 wt. %, preferably 8-20 wt. %. An
35 equilibrium molecular sieve cracking catalyst may

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1 The construction of regeneration zone 26
2 can be made with any material sufficiently able to
3 withstand the relatively high temperatures involved
4 when afterburning is encountered within the vessel
5 and the high attrition conditions which are inherent
6 in systems wherein fluidized catalyst is regenerated
7 and transported. Specifically, metals are contemplated
8 which may or may not be lined. More specifically,
9 ceramic liners are contemplated within
10 any and all portions of the regeneration zone
11 together with alloy use and structural designs in
12 order to withstand temperatures of about 760°C and,
13 for reasonably short periods of time, temperatures
14 which may be as high as 1000°C.

15 The pressure in the regeneration zone is
16 usually maintained in a range from about atmospheric
17 to about 50 psig., preferably from about 10 to 50
18 psig. It is preferred, however, to design the
19 regeneration zone to withstand pressures of up to
20 about 100 psig. Operation of the regeneration zone
21 at increased pressure has the effect of promoting the
22 conversion of carbon monoxide to carbon dioxide and
23 reducing the temperature level within the dense bed
24 phase at which the substantially complete combustion
25 of carbon monoxide can be accomplished. The higher
26 pressure also lowers the equilibrium level of carbon
27 on regenerated catalyst at a given regeneration
28 temperature.

29 The residence time of the spent catalyst in
30 the regeneration zone is not critical so long as the
31 carbon on the catalyst is reduced to an acceptable
32 level. In general, it can vary from about 1 to
33 30 minutes. The contact time or residence time of
34 the flue gas in the dilute catalyst phase establishes
35 the extent to which the combustion reaction can reach

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1 contain as little as about 1 wt. % crystalline
2 material. Admixtures of clay-extended aluminas may
3 also be employed. Such catalysts may be prepared in
4 any suitable method such as by impregnation, milling,
5 co-gelling, and the like, subject only to the provision
6 that the finished catalyst be in a physical
7 form capable of fluidization. In the following tests
8 a commercially available silica alumina zeolite
9 catalyst sold under the tradename CBZ-1, manufactured
10 by Davison Division, W. R. Grace & Company was used
11 after steaming to simulate the approximate equilibrium
12 activity of the catalyst.

13 Fractionation zone 100, of conventional
14 design, typically is maintained at a top pressure
15 ranging between about 10 and 20 psi and a bottoms
16 temperature ranging up to about 400°C. The specific
17 conditions will be a function of many variables
18 including inlet product composition, inlet feed rates
19 and desired compositions in the overhead, middle
20 cut and bottoms. The middle cut fed to hydrogenation
21 zone 110 preferably has a boiling range of about 200
22 to about 370°C and is frequently referred to as a
23 light cat cycle oil. The feed to the hydrogenation
24 zone, preferably light cat cycle oil, should include
25 compounds which will accept hydrogen in zone 110 and
26 readily release the hydrogen in reaction zone 10
27 without dehydrogenative action. Preferred hydrogen
28 donor compounds include two ring naphthenic compounds
29 such as decahydronaphthalene (decalin) and two ring
30 hydroaromatic compounds such as tetrahydronaphthalene
31 (tetralin).

32 Hydrogenation zone 110 may be of conventional
33 design. Typical hydrogenation catalysts
34 include molybdenum salts and nickel and/or cobalt
35 salts deposited on a support material. The residence

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time of the middle cut from zone 100 in the hydrogenation zone may range from about 10 to about 240 minutes, depending on the hydrogen donor, hydrogenation catalyst, operating conditions and the desired degree of hydrogenation.

As shown by the data in Tables I-IX the incorporation of a reduction zone 70 is not effective for passivating a metal contaminated catalyst unless:

A. a temperature in excess of about 500°C is used; and

B. at least two metals selected from the group consisting of nickel, iron and vanadium are utilized.

The data in Table X shows that use of a hydrogen donor also decreases hydrogen and coke makes. When the use of a hydrogen donor is combined with the previously described passivation process, this results in still lower coke makes.

Unless otherwise noted the following test conditions were used. The CBZ-1 catalyst utilized was first steamed at 760°C for 16 hours after which the catalyst was contaminated with the indicated metals by laboratory impregnation followed by calcining in air at about 540°C for four hours. The catalyst was then subjected to the indicated number of redox cycles. Each cycle consisted of a five-minute residence in a hydrogen atmosphere, a five-minute nitrogen flush and then a five-minute residence in an air atmosphere at the indicated temperatures. Following the redox cycles the catalyst was utilized in a microcatalytic cracking (MCC) unit. The MCC unit comprises a captive fluidized bed of catalyst kept at a cracking zone temperature of 500°C. Tests were run by passing a vacuum gas oil having a minimum boiling point of about 340°C

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and a maximum boiling point of about 565°C through the reactor for two minutes and analyzing for hydrogen and coke production. In Table I data is presented illustrating that the incorporation of a reduction step followed by an oxidation step (redox) significantly decreased the hydrogen and coke makes.

TABLE I

	Wt. % Metal on Catalyst			Treatment Prior to Cracking	Yields Wt. % on Feed	
	Ni	V	Fe		H ₂	Coke
12	0.16	0.18		Calined	0.86	7.82
13	0.16	0.18		Redox 650°C	0.62	6.04
14	0.12	0.12		Calined	0.53	5.49
15	0.12	0.12		Redox 650°C	0.34	4.15
16	0.15	0.19	0.35	Calined	1.16	10.61
17	0.15	0.19	0.35	Redox 650°C	0.79	7.48

Table II illustrates that hydrogen and coke make reductions similar to that shown in Table I also were obtained on a metals contaminated catalyst wherein the metals had been deposited by the processing of heavy metal containing feeds rather than by laboratory impregnation.

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TABLE II

	Wt. % Metal on Catalyst			Treatment	Yields Wt. % on Feed	
	Ni	V	Fe		H ₂	Coke
5	0.28	0.31	0.57	510°C Cracking 620°C Regen. (Many cycles)	1.13	9.11
10	0.28	0.31	0.57	Redox 650°C 4 cycles	0.75	5.41
12	0.26	0.29	0.36	510°C Cracking 707°C Regen. (Many cycles)	0.73	6.05
15	0.26	0.29	0.36	Redox 650°C 4 cycles	0.53	3.94

Table III illustrates that the degree of passivation is a function of the reduction zone temperature. It can be seen that the adverse catalytic effects of the metal contaminants are only slightly reduced over that of untreated catalyst, where the temperature in reduction zone 70 is only 500°C. As the reduction zone temperature is increased, it can be seen that the degree of passivation increases.

TABLE III

26					Yields Wt. %
27	Wt. % Metal	Redox			on Fe
28	on Catalyst	Treatment Temp. °C		H ₂	Coke
29	0.28Ni, 0.31V, 0.57Fe	No Redox Treatment	1.13	9.11	
30		500	1.10	8.55	
31		600	0.99	7.94	
32		625	0.98	7.33	
33		650	0.75	5.41	
34		700	0.59	4.80	
35		750	0.50	4.11	

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Based on this data, it is believed that the reduction step decreases the hydrogen and coke makes and that the reduction must be performed at a temperature in excess of 500°C.

Table IV, illustrates that where only one of the metal contaminants is present, the redox step at 650°C is not effective in reducing the hydrogen and coke makes.

TABLE IV

	Wt. % Metal on Catalyst			Treatment Prior To Cracking	Yields, Wt. % on Feed	
	Ni	V	Fe		H ₂	Coke
13	0.21			Calined	0.80	8.10
14	0.21			Redox 650°C 4 cycles	0.72	7.96
16		0.29		Calined	0.38	3.88
17		0.29		Redox 650°C 4 cycles	0.36	4.20

Thus, to passivate the metal contaminants on a catalyst, where at least a major portion i.e., at least 50 wt. % of the total of the metal contaminants comprises nickel, vanadium or iron, it may be necessary to add predetermined quantities of either of the other two contaminants. Typically, crude oil will not contain relative high concentrations of iron. Vanadium and nickel, however, typically are found in many crudes, with the relative amounts varying with the type of crude. For example, certain Venezuelan crudes have relatively high vanadium and relatively low nickel concentrations, while the converse is true for certain domestic crudes. In addition, certain hydrotreated residual oils and hydrotreated gas oils may have relatively high nickel

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1 and relatively low vanadium concentrations, since
2 hydrotreating removes vanadium more effectively than
3 nickel. A catalyst could have substantial iron
4 depositions where the iron oxide scale on process
5 equipment upstream of the catalyst breaks off and
6 is transported through the system by the feedstock.
7 The relative catalytic activity of the individual
8 metal contaminants nickel, vanadium and iron for the
9 formation of hydrogen and coke are approximately 10:
10 2.5: 1. Based on this, iron preferably should be
11 added to passivate catalyst contaminated only with
12 nickel, or vanadium. Table V illustrates the passi-
13 vation that is achieved by adding quantities of
14 iron to catalyst comprising only vanadium or only
15 nickel.

TABLE V

Wt. % Metal on Catalyst	Treatment Prior To Cracking	Yield, Wt. % on Feed	
		H ₂	Coke
0.17 Ni	Calcined	0.76	7.30
0.17 Ni, 0.23 Fe	Redox 650°C 4 cycles	0.51	5.27
0.29 V	Calcined	0.38	3.88
0.29 V, 0.13 Fe	Redox 650°C 4 cycles	0.30	3.72

16 Table VI illustrates the passivation
17 achieved by adding varying weights of vanadium to
18 catalyst comprising only the nickel contaminant.
19 Attention is directed to the fact that the addition
20 of 0.02 wt. % vanadium followed by redox partially
21 passivated the catalyst. Combination of the nickel
22 contaminated catalyst with 0.12 wt. % vanadium
23 followed by redox further passivated the catalyst.
24 However, combination of the nickel contaminated

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1 catalyst with 0.50 wt. % vanadium resulted in an
2 increase in undesired catalytic activity over that of
3 the catalyst containing only 0.12 wt. % nickel.
4 Thus, there appears to be a level of addition of the
5 second metal component, above which the effectiveness
6 of the passivation decreases. The exact amount of
7 nickel, vanadium or iron which should be added to a
8 metal-contaminated catalyst has not been determined.

TABLE VI

Wt. % Metal on Catalyst	Treatment Prior To Cracking	Yields, Wt. % on Feed	
		H ₂	Coke
0.12	Calcined	0.60	5.65
0.12	Redox 650°C 4 cycles	0.44	4.78
0.12 0.02	Redox 650°C 4 cycles	0.39	4.53
0.12 0.12	Redox 650°C 4 cycles	0.34	4.15
0.12 0.50	Calcined	1.17	11.08
0.12 0.50	Redox 650°C 4 cycles	0.72	6.86

23 Table VII illustrates passivation of a
24 catalyst impregnated with equal weight percentages of
25 nickel and vanadium. It should be noted that the
26 redox at 650°C resulted in a significant decrease
27 in hydrogen and coke makes, but that, here also, the
28 further addition of passivating metal in the form of
29 iron actually increased the undesired catalytic
30 activity of the metal contaminants slightly.

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TABLE VII

Wt. % Metal on Catalyst	Treatment Prior To Cracking	Yields, Wt. % on Feed	
		H ₂	Coke
0.12 0.12	Calcined	0.53	5.49
0.12 0.12	Redox 650°C 4 cycles	0.34	4.15
0.12 0.12 0.26	Redox 650°C 4 cycles	0.37	4.50

10 Table VIII illustrates that metals-contam-
11 inated catalyst also can be passivated by the use of
12 carbon monoxide rather than hydrogen as the reducing
13 agent. In one run CP* grade CO containing 99.3% CO by
14 volume was utilized in the previously described
15 passivation process while reagent grade hydrogen was
16 used in the comparative run. It can be seen that
17 both reducing agents passivated the catalyst to about
18 the same extent.

TABLE VIII

Wt. % Metal on Catalyst	Treatment Prior To Cracking	Yields, Wt. % on Feed	
		H ₂	Coke
0.28 0.31 0.57	Calcined	1.13	9.11
	Redox 650°C 4 cycles, H ₂	0.75	5.41
	Redox 650°C 4 cycles, CO	0.73	5.83

28 As shown by the data of Table IX, the
29 addition of iron or antimony followed by high temper-
30 ature redox, reduced the rate of hydrogen and coke
31 formation. The addition of both iron and antimony
32 followed by high temperature redox leads to a still greater
33 decrease in hydrogen and coke makes.

* Chemically Pure

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TABLE IX

Wt. % Metal on Catalyst	Treatment Prior To Cracking	Yields, Wt. % on Feed	
		H ₂	Coke
0.17 Ni	Calcined	0.76	7.30
0.17 Ni, 0.23 Fe	Redox 650°C 4 cycles	0.51	5.27
0.27 Ni	Calcined	0.83	8.40
0.27 Ni, 0.52 Sb	Redox 650°C 4 cycles	0.59	6.03
0.27 Ni, 0.52 Sb, 0.34 Fe	Redox 650°C 4 cycles	0.54	5.31

13 In addition to antimony, it is believed that other
14 known passivation agents such as tin, bismuth and
15 manganese in place of the antimony also would
16 decrease the hydrogen and coke makes.

17 It has been found that one passage through
18 the reaction and regeneration zones reduces the
19 effectiveness of the reduction zone passivation.
20 Thus, at least a portion of the catalyst preferably
21 is passed through reduction zone 70 on every catalyst
22 regeneration cycle.

23 The quantity of metal contaminant, or
24 passivation promoter, if any, that should be added to
25 the system may be determined preferably by monitoring
26 the hydrogen and coke makes in the reaction zone or
27 by analyzing the metal contaminant concentration
28 either in the hydrocarbon feed or on the catalyst.
29 Where additional iron, vanadium or nickel is to be
30 added to the system to reduce the hydrogen and coke
31 makes, it is believed that the additional quantities
32 of these metals should be added to the feed, rather
33 than impregnated onto the catalyst prior to use.
34 Impregnation of an excess of these metals onto the
35 catalyst prior to use in the cracking operation
36 may lead to higher initial hydrogen and coke makes.

Moreover, where passivation promoters having relatively high vapor pressures, such as antimony, are used, some of the passivation promoter may be lost to the atmosphere if it is impregnated onto the catalyst. It has been found that the passivation efficiency of antimony is higher when the antimony is incorporated into the hydrocarbon feedstock than when it is impregnated onto the catalyst.

Table X shows that the addition of a hydrogen donor to the reaction zone reduces the hydrogen and coke makes. When this is combined with the previously described passivation process, still lower coke makes result. In Table X the feed for all tests was 60% vacuum gas oil (VGO), and 40% light cat cycle oil (LCCO). The vacuum gas oil had a minimum boiling point of about 340°C and a maximum boiling point of about 565°C as in the previous tests. The light cat cycle oil had a minimum boiling point of about 200°C and a maximum boiling point of about 325°C. In the first test shown in Table X the LCCO was not hydrogenated and the metals contaminated catalyst was not passivated. In the second test the LCCO fraction of the feed was hydrogenated by passing the LCCO through a hydrogenation zone maintained at a temperature of about 371°C and 2000 psig, comprising a nickel-molybdenum sulfided catalyst in a carbonaceous matrix to increase the hydrogen content of the LCCO fraction from 10.51 wt. % hydrogen to 12.10 wt. % hydrogen. The average residence time of the LCCO in the hydrogenation zone was about 180 minutes. In the third test, the LCCO fraction of the feed was not hydrogenated, but the catalyst was passivated by subjecting the catalyst to 4 redox cycles in a hydrogen atmosphere as previously described. In the fourth test the LCCO fraction of

the feed was hydrogenated as in test 2, and the catalyst was passivated as in test 3. It may be seen that the coke make in test 4 was substantially lower than that in tests 1, 2 or 3, thus demonstrating that use of a hydrogen donor material in the feed combined with catalyst passivation decreases the coke make more than either process alone.

TABLE X

Feed Composition-40% LCCO:60%VGO

Test No.	Wt. & Metal on Catalyst			Treatment Prior To Cracking	Yields, Wt. % on Feed	
	Ni	V	Fe		H ₂	Coke
1	0.48	0.61	0.61	No LCCO hydrogenation. No catalyst passivation	1.10	10.10
2				LCCO hydrogenated. No catalyst passivation	1.02	8.16
3				No LCCO hydrogenation. Catalyst passivated. Redox 750°C 4 cycles, H ₂	0.76	6.67
4				LCCO hydrogenated. Catalyst passivated. Redox 750°C 4 cycles, H ₂	0.75	4.60

Although the subject process has been described with reference to a specific embodiment, it will be understood that it is capable of further modification. Any variations, uses or adaptations of

the invention following, in general, the principles of the invention are intended to be covered, including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as fall within the scope of the invention.

In this patent specification, "psi" designates "pounds per square inch" and is converted to the equivalent pressure in kg/cm² by multiplying by 0.07031. "SCF" designates "standard cubic feet", and is converted to litres by multiplying by 28.316.

Velocities in "feet/sec" are converted to cms/sec by multiplying by 30.48, and weights expressed in "tons" are converted to tonnes by multiplying by 0.9072.

Temperatures in °F are converted to °C by subtracting 32 and then dividing by 1.8.

CLAIMS

1. A method of reducing the rate of coke production from a hydrocarbon feedstock (16) which is cracked to lower molecular weight products (52) by contact (10) with a cracking catalyst where the feedstock contains at least two metals selected from nickel, vanadium and iron and where at least some of the said metals become deposited on the catalyst as contaminants and where the catalyst is periodically subjected to a regeneration treatment (26) in the absence of hydrocarbon feedstock, characterized in that after the regeneration treatment (26) and before contact (10) with hydrocarbon feedstock (16), the catalyst is subjected to a reduction treatment (70) at an elevated temperature for a time which is sufficient to at least partially passivate the metal contaminants on the catalyst.

2. The method of claim 1 in which the reduction treatment (70) is performed at a temperature above 600°C.

3. The method of either claim 1 or claim 2 in which at least 50 weight percent of the total of said metal contaminants deposited on the catalyst comprises only one of said metal contaminants.

4. The method of any one of claims 1 to 3 comprising the steps of:

(a) monitoring the composition of the metal contaminant deposited on the catalyst; and

(b) adding an effective amount of one of said metal contaminants not present as the major contaminant on the catalyst.

5. The method of any one of claims 1 to 4 in which the catalyst is subjected to the reduction treatment (70) for a time or an average time in the range of from 10 to 240 minutes.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C., 2 de enero de 2008

Abogado
EMILIO FERRERO
Apoderado

ASUNTO	Radicación	04-1078
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	350
	Folios	026

Patente de Invención	☒	Patente de Modelo de Utilidad	☐
Vía Nacional	☐		
Vía PCT (fase nacional)	☒	Cap. I	☐
		Cap. II	☒

No. Sol. Internacional	<u>PCT/US02/23243</u>
Fecha de Presentación Internal.	<u>9 de julio de 2002</u>

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- 1.1. Descripción: Folios: 48 a 94
- 1.2. Reivindicaciones: Folios: 95 a 102 como se radicó inicialmente
Folios: 168 a 172 modificadas
- 1.3. Prioridad: Folios: 35 a 47
(10 de julio de 2001, Estados Unidos No. 09/901,939)
- 1.4. Oficio No. 10202: Folios: 144 a 160
- 1.5. Rta. del solicitante Folios: 161 a 165

2. Objeto de la invención

- El Título de la solicitud es: **"REDUCCION DEL AZUFRE EN LA GASOLINA EN EL CRAQUEO CATALITICO FLUIDO"** (Folio 2).
- Esta invención se relaciona con la reducción del azufre en la gasolina y otros productos del petróleo producidos por un proceso de craqueo catalítico. En particular esta invención se relaciona con un proceso de craqueo catalítico mejorado, el cual suministra corrientes de producto de craqueo catalítico de fracciones de gasolina liviana y pesada que tienen un contenido en azufre reducido.

En la **reivindicación independiente 1** se define un proceso para reducir el contenido de azufre de productos de craqueo líquido de un proceso de craqueo catalítico fluido (FCC) en el cual una alimentación de hidrocarburo pesado que comprende compuestos de órgano azufre es catalíticamente craqueado a productos más ligeros mediante el contacto en un proceso de craqueo de recirculación de catalizador cíclico con un inventario de catalizador de equilibrio de craqueo catalítico fluidizable circulante, el proceso comprende:

- (i) Suministrar una corriente de alimentación de hidrocarburo pesado sustancialmente líquido que comprende por lo menos un compuesto de órgano azufre como una impureza;
- (ii) Introducir una corriente de alimentación de hidrocarburo en la unidad del reactor FCC que opera bajo condiciones de craqueo catalítico y que comprende un inventario circulante de una composición de catalizador en equilibrio;
- (iii) Remover una porción del inventario de catalizador de equilibrio de la unidad del reactor FCC mientras se reemplazan todos los inventarios de catalizador en equilibrio removidos de la unidad con el catalizador fresco para crear un ambiente de régimen estable estacionario dentro de la unidad del reactor FCC;
- (iv) Poner en contacto la corriente de alimentación de hidrocarburo con un compuesto que consiste esencialmente de por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar selectivamente la concentración de vanadio en o sobre el inventario de catalizador en equilibrio por aproximadamente 100 a aproximadamente 20000 ppm, con relación a la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador en equilibrio; y
- (v) Poner en contacto el inventario de catalizador en equilibrio en la unidad del reactor FCC con la corriente de alimentación de hidrocarburo que contiene vanadio bajo un ambiente de régimen estacionario para producir un efluente de la zona de craqueo que comprende productos craqueados líquidos, incluyendo gasolina, que tiene un contenido de azufre reducido.

En la **reivindicación independiente 12** se plantea un proceso mejorado para el craqueo catalítico de una fuente de alimentación de hidrocarburo que contiene por lo menos un compuesto de azufre orgánico que comprende poner en contacto en un reactor de craqueo catalítico fluido (FCC) un inventario del catalizador en equilibrio de craqueo catalítico fluido, removiendo una porción del inventario del catalizador aunque reemplazando la misma cantidad de la composición de catalizador fresco para suministrar un ambiente de régimen estacionario dentro del reactor FCC, la mejora comprende:

- (i) Poner en contacto la alimentación de hidrocarburo con un compuesto de material que consiste esencialmente de por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar selectivamente la concentración del vanadio en o sobre el inventario de catalizador en equilibrio por aproximadamente 100 a aproximadamente 20000 ppm con relación a la cantidad del vanadio inicialmente presente en o sobre el inventario de catalizador en equilibrio;
 - (ii) Poner en contacto de inventario de catalizador en equilibrio con la alimentación de hidrocarburo que contiene vanadio en una unidad del reactor FCC bajo un ambiente de régimen estacionario para producir un efluente de zona de craqueo que comprende productos craqueados líquidos que incluyen gasolina, que tiene un contenido de azufre reducido.
- Con el incremento en las regulaciones ambientales aplicadas a los productos de petróleo, por ejemplo en las regulaciones reformuladas de gasolina (RFG) el contenido de azufre en los productos generalmente ha disminuido en respuesta a las preocupaciones acerca de las emisiones de óxidos de azufre y otros compuestos de azufre al aire luego del proceso de combustión. Por ello, existen diversas propuestas tecnológicas para reducir la concentración de azufre en el proceso de craqueo catalítico FCC sin necesidad de operaciones adicionales. Sin embargo, continúa existiendo la necesidad de encontrar maneras efectivas para reducir el contenido de azufre de la gasolina y de otros productos de craqueo líquido.
 - El objeto de la invención definido se catalogó como **C10G 11/05** y **C10G 11/18**, según la Clasificación Internacional de Patentes (IPC).

3. De la solicitud de Patente

3.1. Descripción (artículo 28 D 486)

- En la descripción de la solicitud en estudio se alude a una figura, no obstante, aunque el señor solicitante allega una (Folio 142), esta no aparece ni en la solicitud original ni en la solicitud internacional. Por lo tanto, se recomienda comentar en el memorial de respuesta la razón de incluir dicha figura que no se presentó en la fase internacional o entonces, retirar la referencia hecha sobre ella en la descripción de la solicitud.
- En conclusión, el capítulo descriptivo no cumpliría con el requisito de claridad como se requiere según el art. 28 de la Decisión 486.

3.2. Reivindicaciones (artículo 30 D 486)

- En la reivindicación independiente 1 se introduce una modificación en la etapa (iv) que es 'poner en contacto la corriente de alimentación de hidrocarburo con **un compuesto que consiste esencialmente de por lo menos un compuesto de vanadio** en una cantidad suficiente para incrementar selectivamente la concentración de vanadio en o sobre el inventario de catalizador en equilibrio por **aproximadamente 100 a aproximadamente 20000 ppm** con relación a la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador en equilibrio' (Negrita Personal).

La expresión 'un compuesto que consiste esencialmente de por lo menos un compuesto de vanadio' es confusa y no es apropiada porque un **compuesto químico** se puede expresar como conformado por elementos químicos, iones, radicales, monómeros cuando son compuestos poliméricos etc., según su naturaleza, pero un compuesto no consiste en otros compuestos.

Ahora bien, las **composiciones químicas** sí están conformadas por compuestos químicos en cantidades posibles de definir. Por esto, se recomienda al señor solicitante corregir la expresión que usa para definir la sustancia que añade a la corriente de alimentación de hidrocarburo, según lo que sustenta en el capítulo descriptivo, y tener en cuenta esto mismo para la reivindicación independiente 12, literal (i).

De otro lado, se recomienda eliminar la expresión ‘aproximadamente’ porque no aporta precisión a la definición del intervalo de concentración pues no se puede definir inequívocamente cuán aproximado o no puede estar un número respecto a los límites del intervalo.

- En las reivindicaciones 6, 7 y 12 también se recomienda eliminar la expresión ‘aproximadamente’ por las mismas razones expuestas en el último párrafo del punto anterior.
- En conclusión, las reivindicaciones 1, 6, 7 y 12 no cumplirían con el requisito de claridad como se requiere según el art. 30 de la Decisión 486.

4. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el Estado de la Técnica es:

Fecha de la solicitud prioritaria: 10 de julio de 2001

- Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes:

N°	Documento	Título	Fecha de Publicación
D1	US4728416	“CRACKING BLENDS OF GAS AND OIL AND RESIDUAL OIL”	1 de marzo de 1988
D2	WO0121733	“REDUCING GASOLINE SULFUR IN FLUID CATALYTIC CRACKING”	29 de marzo de 2001
D3	EP0066018	“METHOD OF REDUCING COKE FORMATION IN HEAVY HYDROCARBON FEED CATALYTIC CRACKING”	8 de diciembre de 1982

- Comentarios sobre el estado de la técnica:

El estado de la técnica definido para el presente caso ha venido evolucionando de forma particular.

En primer lugar, el técnico de nivel medio versado en la materia conoce desde los inicios del craqueo catalítico fluido que la calidad de la carga de hidrocarburos tiene efectos directos sobre el proceso¹. Particularmente, se sabe que las impurezas más importantes que tienen los gasóleos destinados a FCC son nitrógeno, azufre y metales pesados –tales como hierro, **vanadio**, níquel y cobre, pero que estos últimos son contaminantes naturales del crudo que se depositan íntegramente en el catalizador y contribuyen temporal o permanentemente a la desactivación de los catalizadores fluidificados ya que les alteran la selectividad, les reducen la estabilidad o aparecen en los productos como contaminantes indeseables.

¹ MONTGOMERY, J.A. Craqueo Catalítico –Cuarta Parte. El Efecto de la Calidad de la Carga Sobre el Craqueo Catalítico Tipo Fluido. Departamento de Productos Químicos del Petróleo.

Inicialmente se conocía que los metales pesados ocasionaban más producción de hidrógeno y de coque y menos rendimiento de gasolina.

Sin embargo, conforme se evolucionó en el desarrollo de los catalizadores zeolíticos se produjo un salto tecnológico considerable y contrario a la regla técnica hasta el momento conocida, ya que se formularon diversas propuestas de proceso FCC donde los catalizadores de zeolita incluían el vanadio en los tamices moleculares como componente metálico importante que reducía la concentración de azufre de las gasolinas (D2).

Otras propuestas conocidas demuestran que el técnico de nivel medio versado en la materia considera la incorporación de metales pesados como vanadio y níquel en las corrientes de alimentación de gasóleos, generando efectos como la reacción de los metales pesados con los sulfuros de la alimentación logrando así reducir la concentración de azufre en los productos finales y evitando el envenenamiento de los catalizadores con coque (D1 y D3).

Los siguientes resúmenes corresponden a los documentos constituidos como relevantes para el presente caso:

En el documento **US4728416** (D1) se divulga un proceso de craqueo catalítico de mezclas de aceites gaseosos y líquidos pesados de hidrocarburos que contienen cantidades sustanciales de precursores de coque, metales pesados y **compuestos de azufre indeseables**, para obtener fracciones ligeras como por ejemplo gasolina, aceite de calefacción y otros productos. El proceso incluye la regeneración del catalizador por consumo del coque.

En D1 se enseña que es conocida la presencia de azufre en forma elemental de sulfuros y/o sus compuestos en la alimentación hidrocarbonada de procesos FCC y que **el sulfuro y las formas modificadas pueden encontrarse dentro de las gasolinas producidas lo cual es indeseable porque afectan adversamente el índice de octano además que puede ser un contaminante potencial del aire** dado que al quemarse genera dióxido y trióxido de azufre (Columna 8, líneas 9 – 20) (Problema técnico conocido).

El proceso divulgado en D1 se lleva a cabo en una unidad de proceso de craqueo catalítico donde una alimentación hidrocarbonada es craqueada en la zona para ello en condiciones de temperatura y presión aptas para el craqueo en la presencia de un catalizador que es regenerado en una zona de regeneración por quemado del coque, y donde catalizador circula entre la zona de craqueo y la de regeneración; la mejora para obtener un producto comprende introducir suficiente cantidad de materia prima que contiene alta concentración de metales pesados (como vanadio) junto con la alimentación de gas oil en la zona de craqueo para depositar Níquel y Vanadio sobre el catalizador para aumentar el contenido de metales pesados en dicho catalizador hasta un nivel entre 1500 y 6000 ppm y mantener dicho nivel retirando catalizador con vanadio hacia la zona de regeneración (Columna 39, reivindicación 1).

En D1, se realiza el procesamiento de materiales de alimentación que contienen metales sustancialmente en exceso del valor convencional y que por lo tanto tienen un potencial significativamente mayor para acumularse sobre un catalizador y contaminarlo pues es normal que se produzca deshidrogenación, condensación de aromáticos, producción de gas o formación de coque. La acumulación de metales normalmente se considera como inconveniente para el procesamiento FCC pero en la propuesta de D1 se cambia la regla normal de trabajo.

El azufre que contiene normalmente la alimentación inhibe la actividad de los metales pesados manteniendo por ejemplo el vanadio en forma de sulfuro que es menos activo que los metales mismos y así se evitan reacciones de deshidrogenación y coquificación, pero a la vez, se reduce la concentración de azufre en los productos livianos (gasolinas).

En el documento **WO0121733** (D2) se divulga un proceso de craqueo catalítico reformado capaz de mejorar la reducción del contenido de azufre en los productos líquidos del proceso de craqueo, incluyendo la gasolina y las fracciones medias de la destilación. **En este proceso se usan catalizadores de reducción de azufre que llevan un componente metálico que reduce el contenido de azufre en los productos y que comprende vanadio en un estado de oxidación superior a cero.** El componente reductor de azufre incluye un tamiz molecular que contiene el componente metálico dentro de la estructura porosa del tamiz (D2; Resumen de la invención).

En D2 se enseña que el proceso de craqueo catalítico fluido es un proceso convencional que emplea catalizadores basados en zeolita con un componente de craqueo tipo faujasita. Por lo general, en un proceso convencional de craqueo catalítico de lecho fluido, la alimentación de hidrocarburos pesados que contiene los compuestos organosulfurados se fracciona en productos más ligeros, poniendo en contacto dicha alimentación —en un proceso cíclico de craqueo con recirculación de catalizador— con un material catalítico de craqueo fluidizable y circulante particulado.

Las etapas importantes del proceso cíclico son:

- (i) La alimentación se fracciona catalíticamente en una zona de craqueo catalítico poniéndola en contacto con una fuente de catalizador regenerado caliente (catalizador de equilibrio) a fin de producir un efluente formado por productos fraccionados y catalizador usado que contiene coque e hidrocarburos separables por arrastre;
- (ii) El efluente se descarga y se separa, habitualmente mediante uno o más ciclones en una fase vapor rica en los productos de craqueo y en una fase rica en sólidos que lleva el catalizador usado;
- (iii) La fase vapor se extrae como producto y se fracciona en la columna principal del FCC y en sus columnas secundarias para obtener productos de craqueo líquidos incluyendo gasolinas;
- (iv) El catalizador usado se arrastra normalmente con vapor para eliminar los hidrocarburos ocluidos en él, tras lo cual, se regenera por oxidación para producir catalizador en equilibrio que luego se recicla a la zona de craqueo donde se tratan nuevas cantidades de alimentación

En el documento **EP0066018** (D3) se divulga un método para reducir la actividad catalítica de los metales contaminantes sobre catalizadores zeolíticos y para reducir la formación de coque e hidrógeno sobre estos en procesos convencionales de craqueo catalítico fluido.

En D3 se enseña que aunque existen corrientes de hidrocarburos de gran contenido de contaminantes como por ejemplo, vanadio, níquel y hierro, es posible incorporar por ejemplo, vanadio adicional a la alimentación de hidrocarburo carbometálico en lugar de impregnarlo sobre el catalizador previo a su uso (D3, página 23, líneas 29 – 36).

5. Análisis de patentabilidad (artículo 14 D 486)

5.1. Nivel inventivo (artículo 18 D 486)

- El técnico de nivel medio versado en la materia encargado de resolver el problema técnico puede ser un ingeniero químico que labore en la industria petroquímica y que atiende a planes de mejoramiento normalmente formulados en las empresas.
- De acuerdo con las reivindicaciones de la solicitud en estudio se entiende que el principio técnico sobre el cual se fundamenta la propuesta consiste en poner en contacto una corriente de alimentación de hidrocarburo con un compuesto que consiste esencialmente de vanadio en cantidad suficiente para incrementar selectivamente la concentración de vanadio en o sobre el inventario de catalizador en equilibrio por 100 a 20000 ppm con relación a la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador en equilibrio, en el proceso FCC. Sin embargo, en D1 (documento más próximo) se enseña que en procesos FCC convencionales se puede introducir suficiente cantidad de materia prima que contiene alta concentración de metales pesados como el vanadio, junto con la alimentación de gas oil en la zona de craqueo para igualmente depositar metales pesados como Níquel y Vanadio sobre el catalizador y así aumentar el contenido de metales pesados en el catalizador hasta un nivel entre 1500 y 6000 ppm.

Una diferencia encontrada entre el proceso de la solicitud en estudio y el divulgado en D1 es que en el primero, la corriente de alimentación de hidrocarburo se pone en contacto con un compuesto que consiste esencialmente de por lo menos un compuesto de vanadio para incrementar selectivamente la concentración de vanadio en o sobre el inventario de catalizador en equilibrio, mientras que en D1 se pone en contacto con una materia prima que contiene Níquel y Vanadio. Además, en D1 no hay mención específica de las condiciones en que se ponen en contacto las corrientes. Sin embargo, en D2 o D3 se encuentran enseñanzas orientadas a preferir el Vanadio como componente metálico de interés (Ver resúmenes incluidos en el numeral 4 de la presente comunicación) y a incluir dicho componente de vanadio adicional a la alimentación de hidrocarburo carbometálico en lugar de impregnarlo sobre el catalizador previo a su uso (Ver D3).

El técnico de nivel medio versado en la materia con acceso a D1 y D2 o D3, se vería impulsado a desarrollar procesos económicos donde incluir vanadio en las operaciones de craqueo catalítico fluido (FCC) genera dos efectos técnicos: reducir la concentración de sulfuro en las gasolinas y reducir la hidrogenación y formación de coque sobre el catalizador. Estos dos efectos son simultáneos y conocidos porque el contenido de azufre en la alimentación reacciona con el vanadio, produciendo sulfuros que se pueden retirar de las corrientes junto con el catalizador y reduciendo así la concentración total de azufre en los productos finales, además de impedir el envenenamiento del catalizador por formación de coque.

Así las cosas, el proceso propuesto de la solicitud en estudio no generaría un efecto sorprendente que evidencie un salto tecnológico respecto a lo conocido en el arte previo. Por lo tanto, no cumpliría con el requisito de nivel inventivo como se requiere según el art. 18 de la Decisión 486.

6. Respuesta a los argumentos del señor solicitante

La Oficina desea mencionar que D1 sí contiene enseñanzas sobre la reducción de azufre de productos líquidos del proceso FCC:

En D1 se enseña que es conocida la presencia de azufre en forma elemental de sulfuros y/o sus compuestos en la alimentación hidrocarbonada de procesos FCC y que **el sulfuro y las formas modificadas pueden encontrarse dentro de las gasolinas producidas lo cual es indeseable porque afectan adversamente el índice de octano además que puede ser un contaminante potencial del aire** dado que al quemarse genera dióxido y trióxido de azufre (Problema técnico conocido).

El azufre que contiene normalmente la alimentación inhibe la actividad de los metales pesados manteniendo por ejemplo el vanadio en forma de sulfuro que es menos activo que los metales mismos y así se evitan reacciones de deshidrogenación y coquificación, pero a la vez, se reduce la concentración de azufre en los productos livianos (gasolinas) (D1; columna 8, líneas 9 – 30).

Teniendo en cuenta lo anterior, un técnico de nivel medio versado en la materia sabe que al añadir mayor concentración de vanadio se producen dos efectos, uno que la concentración de azufre en las gasolinas se reduce por la reacción de estos con el componente metálico depositado en el catalizador y dos, que se reduce la formación de coque que envenena las zeolitas.

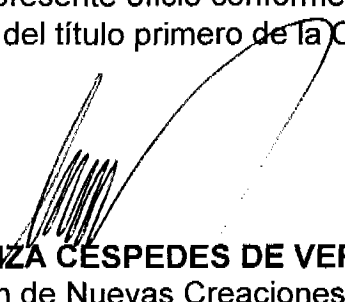
7. Conclusión

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	US4728416	1 – 13	Nivel Inventivo
D2	WO0121733 ó		
D3	EP0066018		

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de **60 días** contados a partir de la fecha de notificación de la presente comunicación. **En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.**

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha _____

CONCEPTO TÉCNICO No. 2602	EXAMINADOR TÉCNICO Código No. 202042
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