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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 respectivamente Direcciones 7500 Grace Drive Columbia Maryland 21046 y 3275 Gallows Road Fairfax Virginia 22037 Estados Unidos de América respectivamente Teléfono 46 09 70 E mail clientes@camyp.com Fax 249 40 70 Domicilios Columbia Maryland y Fairfax Virginia Estados Unidos de América respectivamente	IDENTIFICACION C C ☐ NIT ☐ C E ☐ Otro ☐ Numero _____
3 REPRESENTANTE O APODERADO	Nombre Emilio FERRERO Dirección Carrera 4ª No 72-35 Teléfono 347 36 11 E mail cavelier@cavelier.com Fax 217 92 11 Domicilio Bogotá Colombia	IDENTIFICACION C C ☒ NIT ☐ C E ☐ Otro ☐ Numero 438 019 TP 31 929
4 Numero de expediente 04 001 078 Clase C20G 011/005 Titulo del Invento REDUCCIÓN DEL AZUFRE EN LA GASOLINA EN EL CRAQUEO CATALITICO FLUIDO		
5 Descripcion de la correccion o modificación solicitada Presento con este formato la Figura unica mencionada en la descripción de la presente invención La presente Figura no implica una ampliación de la invención originalmente presentada pues se encuentra soportada totalmente en la descripción		
6 Comprobante de pago No 04 - 12 039 Fecha 16 de febrero de 2004		
7 Anexos ☒ Comprobante de pago de la tasa por \$ 87 000 oo ☐ Poderes si fuere el caso ☐ Certificado de existencia y representación legal cuando el solicitante sea persona jurídica		

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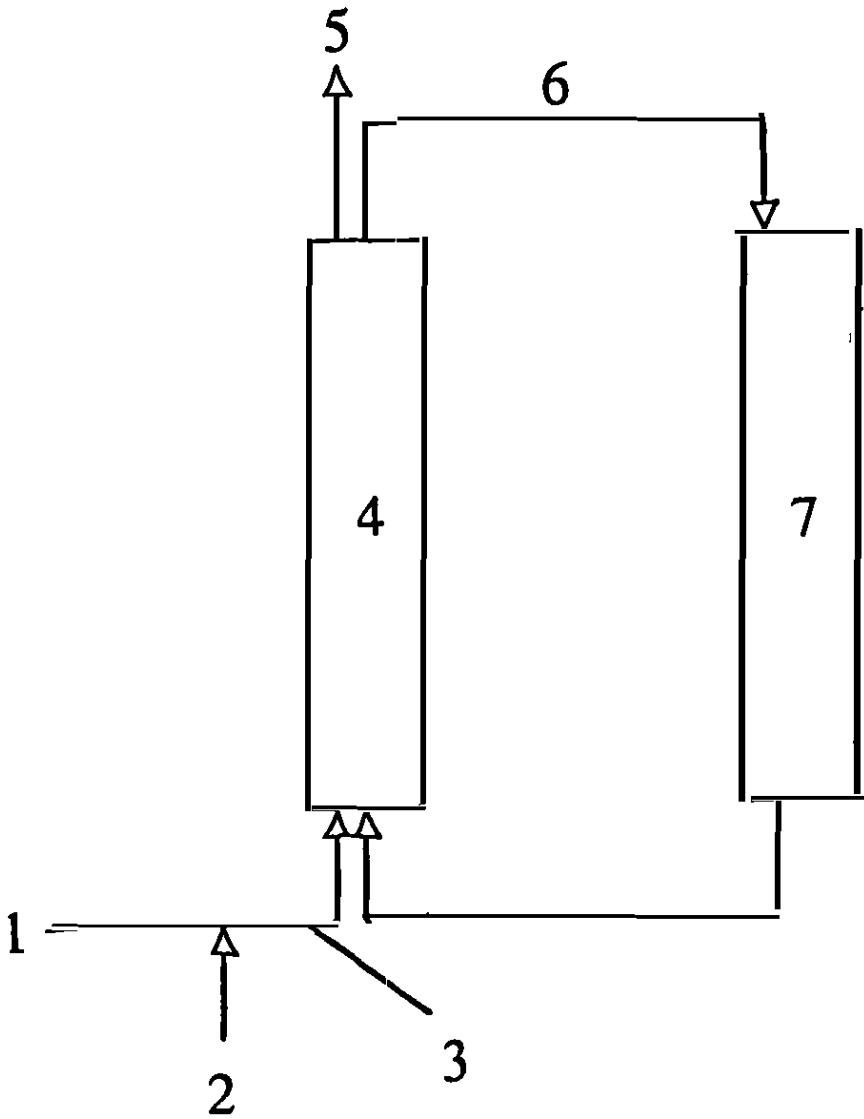
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FIGURA



United States Patent (19)

Myers, deceased

(11) Patent Number 4,728,416
(43) Date of Patent: Mar 1, 1988

[54] CRACKING BLEND OF GAS OIL AND
RESIDUAL OIL

[72] Inventor: George D. Myers, deceased, late of
Ashland, Ky. by Virginia K. Myers,
administratrix

[73] Assignee: Ashland Oil, Inc., Ashland, Ky

[21] Appl. No. 238,264

[22] Filed: Apr 28, 1981

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 94,216, Nov. 14, 1979,
Pat. No. 4,341,624 and continuation-in-part of Ser.
No. 94,092, Nov. 14, 1979, Pat. No. 4,332,872, and
continuation-in-part of Ser. No. 346,751 Mar. 23, 1981
Pat. No. 4,374,696, and continuation-in-part of Ser.
No. 346,762, Mar. 23, 1981, Pat. No. 4,375,904, and
continuation-in-part of Ser. No. 346,791 Mar. 23, 1981
Pat. No. 4,374,626.

[31] Int. Cl. C10G 11/02
[32] U.S. Cl. 308/120
[36] Field of Search 308/120

Reference Cited

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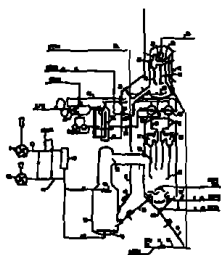
3,944,482 5/1978 Mitchell et al. 308/120
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Primary Examiner—Curtis R. Davis
Attorney Agent, or Firm—Richard C. Wilcox, Jr.
Donald S. Zinn

[57] (ABSTRACT)

A process is disclosed for the catalytic cracking of gas
oil with an additional nickel and vanadium metals con-
taining heavy feedstock. Included is regeneration of the
catalyst by burning off coke.

19 Claims, 3 Drawing Figures



U.S. Patent Mar 1 1988

Sheet 1 of 2

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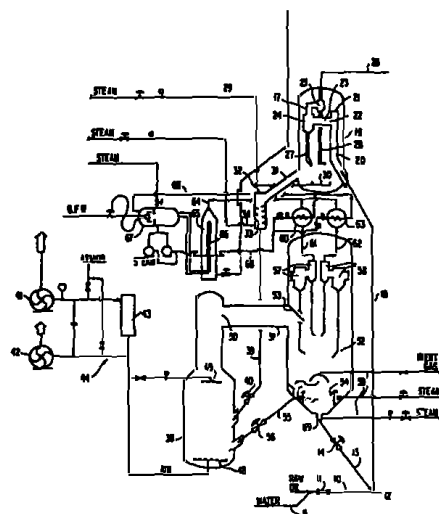


FIG 1

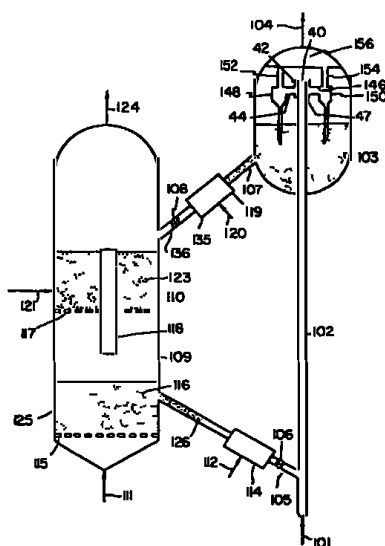


FIG 2

1 CRACKING BLENDS OF GAS OIL AND RESIDUAL OIL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of the following pending U.S. applications filed in the name of the inventor herein, Ser. No. 094,214, now U.S. Pat. No. 4,344,634, and Ser. No. 094,052, now U.S. Pat. No. 4,332,673, both filed Nov. 14, 1979, and Ser. No. 246,731 now U.S. Pat. No. 4,376,696, and Ser. No. 246,782, now U.S. Pat. No. 4,372,404, and Ser. No. 246,791 now U.S. Pat. No. 4,376,038 all filed Mar. 23, 1981 the entire disclosures of each of the aforementioned applications hereby being incorporated herein by reference.

TECHNICAL FIELD

This invention relates to fluid catalytic cracking of blends of gas oils and residual oils into lighter fractions, which may for example include gasoline, heating oil and/or other products.

BACKGROUND ART

In this art, as fluid catalytic cracking is an elevated temperature process, the cracking of a cracking catalyst. The cracking reaction tends to deposit coke on the catalyst. Thus, at the conclusion of the cracking reaction the resultant vapor products are separated from the catalyst particles and the latter are regenerated in a regeneration zone by burning coke off of the catalyst. The catalyst is circulated between the cracking zone and the regeneration zone, whereby coke-laden spent catalyst separated from the products is delivered to the regeneration zone for regeneration, and regenerated catalyst, freed of its coke deposit and discharged from the regeneration zone, is returned to the cracking zone for contact with additional gas oil feed. Many suitable types of apparatus for performing such reactions are known to persons skilled in the art. For a number of examples see U.S. Pat. No. 4,201,530, columns 1 thru 45-46. See also U.S. Pat. No. 4,056,333 and 4,070,159 to George D. Myers, et al.

The gas oil feed conventionally employed in fluid catalytic cracking typically comprise virgin gas oils, recycled streams from fluid catalytic cracking and thermally cracked material boiling below about 1050° F typically in the range of about 600° F to about 1050° F and more typically less than 1025° F or in many cases less than 1000° F. All of these feeds typically contain rather small amounts of heavy metals such as nickel and vanadium, which are understood to be present in the form of high molecular weight organo-metallic compounds. The quantity of such metals present in the feeds may for example be expressed in terms of equivalent nickel, which is the total amount of metal (Ni) content plus 20% of the vanadium (V) content of the feed, i.e., $Ni + V/5$.

During the course of the cracking reaction the above-mentioned metals are deposited on the circulating catalyst. During the life of a given catalyst particle, as it repeatedly is exposed to feed, the accumulation of metallic nickel and vanadium thereon progressively increases. Occasionally speaking the operation of fluid catalytic cracking units practice continuous or intermittent introduction of fresh catalyst to the unit to make up for any losses of catalyst from the system and/or to assist in

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maintaining the desired level of catalytic activity in the catalyst inventory. As persons skilled in the art will readily appreciate, the nickel and vanadium accumulation may vary from one particle to another within the inventory but the overall or average inventory of metals on catalyst is in general a function of the amount of such metals present on the fresh catalyst added to the system, the amount of such metals present in the feeds supplied to the system, the relative quantities in which feed and catalyst are brought into contact with one another over an extended period of operation, and the amount of catalyst introduction and withdrawal (if any) which occurs during such operating period. It has been reported that in typical fluid catalytic cracking operations the process is controlled in such a manner as to cause the metal content of the catalyst to equilibrate at a level in the range of about 200 to about 1400 parts per million based on the weight of the catalyst.

Heretofore the present inventor has in certain applications filed in the sole name of the present inventor and jointly with Lloyd E. Busch, described the RCC process, a process of fluid catalytic conversion of carbonaceous oils to liquid products similar to those obtained in FCC processes. The RCC process is for example disclosed in U.S. Pat. Nos. 4,341,634, 4,347,122, 4,339,687, 4,334,933 and 4,334,673 the entire disclosures of which are hereby incorporated by reference. In RCC processing the feed as a whole will normally contain substantial proportions of components which will not boil below 1035° F or 1050° F. Such high boiling components generally impart to the carbonaceous oil feeds considerably higher Carbonium or Ramothston carbon values than are typical with gas oil feeds. Moreover these higher boiling components are frequently or usually the representatives of the organo-metallic compounds which are the source of the nickel and vanadium contamination of the feed. Thus in carbonaceous oil feeds one will generally find a metals content, expressed in equivalent nickel (see above) or nickel equivalents of at least about 4. Nickel equivalents may be expressed in terms of the equation:

$$\text{Nickel Equivalents} = Ni + \frac{V}{5} + \frac{Co}{10} + \frac{Fe}{10}$$

wherein each of the above indicated metals is expressed in parts by million by weight of such metal, as metal, based on the weight of the feed. Because of the much larger metals contents of carbonaceous oils, they tend to impart to the circulating catalyst inventories substantially higher metals accumulations than are found in FCC processing. For example, the metals accumulations on catalyst may range from substantially in excess of 600 ppm nickel equivalents to as high as 70,000 ppm nickel equivalents. In many instances the nickel equivalents of metals accumulated on the catalyst inventory will exceed 3000 ppm. The continued operating difficulties associated with high metals and coke precursors in feed and high rates of metal and coke deposition on catalyst have represented a severe challenge for refiners.

Standing somewhat as a middle ground between these two extremes is the practice of fluid catalytic cracking blends of gas oil, as above described, with various residual oils, the latter consisting significantly more metals and/or coke precursors than are common in the typical FCC gas oils. For example see U.S. Pat.

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Nos. 3,781,197 and 3,783,959 by Millard C. Bryson et al. These patents disclose the cracking of a gas oil admixed with controlled amounts of residual oils, which may or may not have been hydro-desulfurized, over mobile catalysts. Especially such procedure provides improved yields of gasoline and may improve the clearness value of certain boiling ranges of the resultant liquid fuel, i.e. gasoline, product. The teachings of this art, in connection with prior FCC practice, regard the accumulation of metal on the catalyst as deleterious.

SUMMARY OF THE INVENTION

The present invention comprises an improvement in the known process of catalytic cracking wherein a gas oil feed is cracked in a cracking zone at an elevated temperature in the presence of a cracking catalyst. In accordance with prior procedure the cracking catalyst is regenerated in a regeneration zone by burning coke off of the catalyst, and catalyst is circulated between the cracking zone and the regeneration zone. The present invention is an improvement for obtaining a naphtha product of improved octane number. It comprises introducing a sufficient amount of a nickel and vanadium metal-containing heavy feedstock with the gas oil feed into the cracking zone to deposit nickel and vanadium metals on the catalyst and to raise the nickel and vanadium metals content of the catalyst to a level ranging from about 1500 to about 6000 parts per million of said metals expressed as equivalent nickel, based on the weight of the catalyst. The level of nickel and vanadium metals content of the catalyst is maintained in the aforementioned range by adding low nickel and vanadium metal-containing catalyst to the system, e.g. to the regeneration zone. High nickel and vanadium metal-containing catalyst may be withdrawn from the system if the system losses of catalyst are not sufficient to balance the rate of catalyst addition.

The following are some optional but preferred embodiments of the foregoing general process. For example, the foregoing process may be practiced using a metal-containing heavy feedstock, added to the gas oil feed, which has a final boiling point about 1050° F. This however does not imply that any or all of the materials in the heavy feedstock will boil above 1050° F. since the heavy materials in question may crack before they boil, and some of the feed components may be incapable of boiling. According to another alternative embodiment the metal-containing heavy feedstock may be added to the gas oil feed prior to the introduction of the feed, i.e. the resultant mixture, into the cracking zone. The metal-containing heavy feedstock may for example contain from about 2 to about 1000 ppm of equivalent nickel, based on the weight of said heavy feedstock. Optionally the metal-containing feedstock may be continuously added with the gas oil feed in amounts ranging above 0% to about 25% and higher based on the volume of the gas oil, and fresh catalyst may be added to the unit at a rate of 0.05 pounds to about 0.50 pounds per barrel of gas oil feed processed, and catalyst may be withdrawn at a rate sufficient to maintain the unit in balance. However ratios of heavy feedstock to gas oil feed in excess of 25% ranging as high as 66% or more are contemplated. Accordingly the fresh catalyst addition rate may, if desired, be adjusted upwardly from the range indicated. The option of operating with 0 to 35% heavy feedstock based on gas oil volume may be practiced in conjunction with the use of a gas oil feed boiling within the range of about 800° F. to about 1050°

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F and addition of the metals containing heavy feedstock to the gas oil feed prior to the introduction of the feed into the cracking zone. A preferred range of metals on catalyst ranges from about 2400 to about 4000 ppm expressed as equivalent nickel. The preferred catalysts for carrying out the invention comprise crystalline aluminum silicate zeolites. These and other optional embodiments of the invention are described in greater detail in the accompanying drawings and in the various and preferred embodiments set forth below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of a first form of catalytic cracking unit useful in conducting the process of the present invention.

FIG. 2 is a schematic diagram of a preferred form of apparatus useful for conducting the invention.

BEST AND VARIOUS OTHER ILLUSTRATIVE MODES FOR CARRYING OUT THE INVENTION

The present invention is suitable in providing a simple, relatively straight-forward and highly productive approach to the conversion of gas oil feeds and carbo-metallic oil feeds, such as reduced crudes, to various lighter products such as gasoline. The carbo-metallic feed comprises or is composed of oil which boils above about 600° F. Such oil, or at least the 650° F. + portion thereof, is characterized by heavy metal content of at least about 4, preferably more than about 5, and most preferably at least about 5.5 ppm of nickel equivalents by weight and by a carbon residue on pyrolysis of at least about 1% and more preferably at least about 2% by weight. Two established tests for determining the carbon residue on pyrolysis of a feed are recognized: the Conradson carbon and Ramsbottom carbon tests, the former being described in ASTM D-189-76 and the latter being described in ASTM Test No. D-554-76.

In accordance with the invention, the gas oil feed and carbo-metallic oil feed, in the form of separate or combined streams of pumpable liquid, are brought into contact with hot conversion catalysts in a weight ratio of catalyst to total feed in the range of about 3 to about 16 and preferably more than about 6.

The feed in said mixture undergoes a conversion step which includes cracking while the mixture of feed and catalyst is flowing through a progressive flow type reactor. The feed, catalyst, and other materials may be introduced at one or more points. The reactor includes an elongated reaction chamber which is at least partly vertical or inclined and in which the feed material, resultant products and catalyst are maintained in contact with one another while flowing in a definite phase or stream for a predetermined reactor residence time in the range of about 0.5 to about 10 seconds.

The reaction is conducted at a temperature of about 900° to about 1400° F. measured at the reaction chamber exit, under a total pressure of about 10 to about 30 psia (pounds per square inch absolute) under conditions sufficiently severe to provide a conversion per pass in the range of about 30% or more and to lay down coke on the catalyst in an amount in the range of about 0.3 to about 3% by weight and preferably at least about 0.5%. The overall rate of coke production, based on weight of fresh feed, is at the range of about 4 to about 14% by weight.

At the end of the predetermined residence time, the catalyst is separated from the products, is stripped to

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remove high boiling components and other entrained or adsorbed hydrocarbons and is then regenerated with oxygen-containing combustion-supporting gas under conditions of time, temperature and atmosphere sufficient to reduce the carbon on the regenerated catalyst to about 0.25% or less and preferably about 0.05% or less by weight.

Depending on how the process of the invention is practiced, one or more of the following additional advantages may be realized. If desired, and preferably the process may be operated without added hydrogen in the reaction chamber. If desired, and preferably the process may be operated without prior hydrocracking of the feed and/or without other process of removal of asphaltenes of metals from the feed, and this is true even when the carbo-metallic oil component contains more than about 4, or more than about 5 or even more than about 5.5 ppm Nickel Equivalents by weight of heavy metal and has a carbon residue on pyrolysis greater than about 1%, greater than about 1.5% or greater than about 2% by weight. Moreover all of the conversion feed, as above described, may be cracked in one and the same conversion chamber. The cracking reaction may be carried out with a catalyst which has previously been used (recycled), except for such replacement as required to compensate for normal losses and deactivated catalyst. One measure under the above described conditions. Heavy hydrocarbons not cracked to gasoline in a first pass may be recycled with or without hydrocracking for further cracking in contact with the same kind of feed in which they were first subjected to cracking; condensation, and under the same kind of conditions; but operation is a substantially once-through or single pass mode (e.g. less than about 15% by volume of recycle based on volume of fresh feed) is preferred.

According to one preferred embodiment or aspect of the invention, at the end of the predetermined residence time referred to above, the catalyst is projected in a direction established by the elongated reaction chamber or an extension thereof, while the products, having lower momentum, are caused to make an abrupt change of direction resulting in an abrupt, substantially instantaneous ballistic separation of products from catalyst. The thus separated catalyst is then stripped, regenerated and recycled to the reactor as above described.

According to another preferred embodiment or aspect of the invention, the converter feed contains 650° F. + material which has not been hydrocracked and is characterized in part by containing at least about 5.5 parts per million of nickel equivalents of heavy metals. The converter feed is brought together not only with the above mentioned cracking catalyst, but also with additional gaseous material including steam whereby the resultant separation of catalyst and feed also includes gaseous material wherein the ratio of the partial pressure of the added gaseous material relative to that of the feed is in the range of about 0.25 to about 4. The vapor residence time is in the range of about 0.5 to about 3 seconds when practicing this embodiment or aspect of the invention. This preferred embodiment or aspect and the one referred to in the preceding paragraph may be used in combination with one another or separately.

According to another preferred embodiment or aspect of the invention, the feed material is not only brought into contact with the catalyst, but also with one or more additional materials including particularly liquid water in a weight ratio relative to feed ranging from

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about 0.04 to about 0.25 more preferably about 0.04 to about 0.1 and still more preferably about 0.05 to about 0.15. Such additional materials, including the liquid water may be brought into admixture with the feed prior to, during or after mixing the feed with the aforementioned catalyst, and either after or preferably before, vaporization of the feed. The feed, catalyst and water (e.g. in the form of liquid water or in the form of steam produced by vaporization of liquid water in contact with the feed) are introduced into the progressive flow type reactor which may or may not be a reactor embodying the above described ballistic separation, at one or more points along the reactor. While the mixture of feed, catalyst and steam produced by vaporization of the liquid water flows through the reactor the feed undergoes the above mentioned conversion step which includes cracking. The feed material, catalyst, steam and resultant products are maintained in contact with one another in the above mentioned elongated reaction chamber while flowing in a definite phase or stream for the above mentioned predetermined reactor residence time which is in the range of about 0.5 to about 10 seconds.

The present invention provides a process for the continuous catalytic cracking of a wide variety of feed materials to lower molecular weight products, while maintaining production of highly valuable liquid products, and making it possible, if desired, to avoid vacuum distillation and other expensive treatments such as hydrocracking. The term "value" includes not only these predominantly hydrocarbon components which are liquid at room temperature (i.e. 60° F.), but also those predominantly hydrocarbon components which are gaseous or turn at ambient temperature but liquidify when heated to temperatures in the range of up to about 800° F. The invention is applicable to carbo-metallic oils, whether of petroleum origin or not. For example, provided they have the requisite boiling range, carbon residues on pyrolysis and heavy metals content, the invention may be applied to the processing of such widely diverse materials as heavy bottoms from crude oil heavy biomass crude oil these crude oils known as "heavy crudes" which approximate the properties of reduced crudes, shale oil, tar sand extract, products from coal liquefaction and activated coal, atmospheric and vacuum reduced crudes, extracts and/or bottoms (naffs) from solvent de-asphalting, aromatic extract from lube oil refining, tar bottoms, heavy cycle oil, drop oil, other refinery waste streams and mixtures of the foregoing. Such mixtures can for instance be prepared by mixing available hydrocarbon fractions, including oils, tars, pitches and the like. Also, powdered coal may be suspended in the carbo-metallic oil. Persons skilled in the art are aware of techniques for demetallization of carbo-metallic oils, and demetallized oils may be converted using the invention; but it is an advantage of the invention that it can employ as feedstock carbo-metallic oils that have had no prior demetallization treatment. Likewise, the invention can be applied to hydrocracked feedstocks; but it is an advantage of the invention that it can successfully convert carbo-metallic oils which have had substantially no prior hydrocracking. However the preferred application of the process is to reduced crudes, i.e. that fraction of crude oil boiling at and above 650° F. in admixture with virgin gas oils.

In accordance with the invention one provides carbo-metallic oil feedstock, at least about 70%, more preferably at least about 85% and still more preferably

above 600% (by volume) of which balls are at least 100% (by volume). All balling temperatures herein are based on standard atmospheric pressure conditions. In carbometallic oil partly or wholly composed of material which has been balling at 600°F. + material and 650°F. F material which is 65% of or has been separated from an oil containing components balling above and below 600°F. + material, the terms "balling above" and "650°F. F. + are not intended to imply that all of the material characterized by the term "balling above" and "650°F. F. + is carbometallic oil completely by the invention may contain material which may not ball under any conditions, for example, certain asphalt and asphaltums may crack through balling at 600°F. + and 650°F. F. +.

Thus, for example, when it is said that the fluid components at least about 70% by volume of material which balls above about 650°F. F. it should be understood that the material is not balling at 600°F. F. material which will not ball or volatilize at any temperature. These non-ballable materials when present, may frequently or for the most part be concentrated in portions of the material which ball at 600°F. F. or 650°F. F. or 1025°F. F. or higher. Thus, when it is said that at least about 10% more preferably about 15% and still more preferably at least about 20% (by volume) of the material balls above about 1000°F. F. or 1025°F. F. it should be understood that all or any part of the material not balling below about 1000°F. or 1025°F. F. may or may not be volatile at and above the specified tem-

Preferably the carbo-metallic feeds, or at least the 650° F + material thereto, have a carbon residue on pyrolysis of at least about 2 or greater. For example, the Curadex carbon content may be in the range of about 2 to about 12 and most frequently at least about 4. A particularly common range is about 4 to about 8. Those feeds having a Curadex carbon content greater than about 6 especially need special means for controlling excess heat.

Preferably the cerbo-metallic feed has an average composition characterized by an atomic hydrogen to carbon ratio in the range of about 1.2 to about 1.9 and preferably about 1.3 to about 1.8.

The cerbo-metallic feeds employed in accordance with the invention, or at least the 650° F. + material

therein, may contain at least about 4 parts per million of Nickel Equivalents, as defined above, of which at least about 2 parts per million is nickel (as metal by weight). Carbo-metallic oils within the above range can be prepared from mixtures of two or more oils, some of which do and some of which do not contain the quantities of Ni and Ni equivalents indicated and described above. It should

Nickel Equivalents and nickel set forth above. It should also be noted that the above values for Nickel Equivalents and nickel represent time-weighted averages for a substantial period of operation of the conversion unit, such as one month, for example. It should also be noted that the heavy metals have in certain circumstances exhibited some tendency of increasing tendency after

exhibited some lowering of poisoning tendency after repeated oxidations and reductions on the catalyst, and the literature describes criteria for establishing "effective metal" values. For example, see the article by Cioabai, et al., entitled "Deposited Metals Poison FCC Catalysts" *Oil and Gas Journal*, May 13, 1972, pp 112-121, the contents of which are incorporated herein by reference. If considered necessary or desirable, the contents of Nickel Equivalents and nickel in the carbonyl

metallic oils processed according to the invention may be expressed in terms of "effective metal values." Notwithstanding the gradual reduction in poisoning activity noted by Cimino, et al, the regeneration of catalyst under normal FCC regeneration conditions may not, and usually does not, severely impair the dehydrogenation, desulfurization and aromatic condensation activity of heavy metals accumulated on cracking catalyst.

It is known that about 0.3 to about 5 weight percent of "sulfur" in the form of elemental sulfur and/or its compounds (not reported as elemental sulfur based on the weight of feed) appears in FCC feeds and that the sulfur and modified forms of sulfur can find their way into the resultant gasoline product and, where lead is

added tend to reduce its susceptibility to octane enhancement. Sulfur in the product gasoline often requires sweetening when processing high sulfur containing crudes. To the extent that sulfur is present in the coke, it also represents a potential air pollutant since the regenerator burns it to SO_2 and SO_3 . However, we have

found that in our process the sulfur in the feed is on the other hand able to inhibit heavy metal activity by maintaining metals such as Ni, V, Cu and Fe in the sulfide form in the reactor. These sulfides are much less active than the metals themselves in promoting dehydrogenation and coking reactions. Accordingly it is acceptable

The carbo-metallic oils useful in the invention may and usually do contain significant quantities of co-

pounds containing nitrogen, a substantial portion of which may be basic nitrogen. For example, the total nitrogen content of the crude-oil-metallic oils may be at least about 0.05% by weight. Since cracking catalysts lose their cracking activity to acid sites on the catalyst surface or in its pores, basic nitrogen-containing com-

pounds may temporarily neutralize these sites, poisoning the catalyst. However the catalyst is not permanently damaged since the nitrogen can be burned off the catalyst during regeneration, as a result of which the acidity of the active sites is restored.

quantities of pentane isochlorins, for example at least about 0.5% by weight, and more typically 2% or more or even about 4% or more. These may include for instance asphaltene and other materials.

Alkali and alkaline earth metals generally do not tend to vaporize in large quantities under the distillation conditions employed in distilling crude oil to prepare the vacuum gas oils normally used as FCC feedstocks. Rather these metals remain for the most part in the "bottoms" fraction (the non-vaporized high boiling material which may be further processed in the refinery).

portion) which may for instance be used in the production of asphalt or other by-products. However, residual crude and other carbon-metallic oils are in many cases bottoms products, and therefore may contain significant quantities of alkali and alkaline earth metals such as sodium. These metals deposit upon the catalyst during reaction. Depending on the concentration of the metals

cracking. Depending on the composition of the catalyst and magnitude of the regeneration temperatures to which it is exposed, these metals may undergo interactions and reactions with the catalyst (including the catalyst support) which are not normally experienced in processing VGO under conventional FCC processing conditions. If the catalyst characteristics and regeneration conditions so require, one will of course take the

necessary precautions to limit the amounts of alkali and sodium earth metal in the feed, which must always contain the feed oil or a briquet made with the crude oil in its natural state, as well as components of water steam which are supplied to the cracking unit. Thus, careful dosing of the crude used to prepare the carbonaceous feed may be important when the catalyst is particularly susceptible to alkali and alkaline earth metals. In such circumstances, the content of such metals (hereafter collectively referred to as "sodium") in total feed can be maintained at about 1 ppm or less, based on the weight of the feedstock. Alternatively, the sodium level of the feed may be lowered to that of the catalyst, so as to maintain the sodium level of the feedstock in use substantially the same as or less than that of the replacement catalyst which is charged to the unit.

and.

According to a particularly preferred embodiment of the invention, the carbon-methane oil feedstock consists at least about 70% by volume of material which boils above about 530° F. and at least about 10% of the material which boils above about 550° F. will not test below about 1025° F. The average composition of this feedstock may be of the order characterized by (a) an atomic hydrogen to carbon ratio in the range of about 1.3 to about 1.6; (b) a Conradson carbon value of at least about 2; (c) at least about five parts per million or Nitzsch nitrogen, no defined source, of which is at least about two parts per million is added (see above); (d) at least about one part of chlorine per (c) at least about 0.3% by weight of sulfur; (e) at least about 0.05% by weight of arsenic; and (f) at least about 0.5% by weight of potassium impurities. Very commonly the preferred feed will include all of (i), (ii), (iii), and (iv) and other components found in oils of petroleum and other sources, and will be of the order of the feed conditions providing they do not prevent operation of the process.

Although there is no intention of examining the possibility of using a feedstock which has previously been subjected to some cracking, the present invention has the definite advantage that it can successfully produce large conversions and very substantial yields of liquid hydrocarbon fuels from carbo-mesopile oils which have not been subjected to any substantial amount of cracking. Thus, for example, and preferably at least about 35%, more preferably at least about 50% and most preferably substantially all of the carbo-mesopile feed hydrocarbon feed is processed to produce a liquid hydrocarbon fuel. The process is one in which the cracking conditions are carefully controlled and analyzed under processing conditions. Moreover the process of the invention is suitable for operators in a substantially continuous or single pass mode. Thus, the volume of recycle, if any based on volume of total fresh feed is preferably about 15% or less and more preferably about 10% or less.

In general, the weight ratio of catalyst to total fresh feed (feed which has not previously been exposed to cracking catalyst under cracking conditions) used in the process is in the range of about 3 to about 18. Preferred and more preferred ratios are about 4 to about 12, more

preferably about 5 to about 10 and still more preferably about 6 to about 10, a ratio of about 10 presently being considered most nearly optimum. Within the limitations of product quality requirements, controlling the catalyst to all ratio at relatively low levels within the aforesaid ranges tends to reduce the coke yield of the process, based on fresh feed.

In conventional FCC processing of VGO, the ratio between the number of barrels per day of plant throughput and the total number of tons of catalyst undergoing circulation throughout all phases of the process can vary widely. For purposes of this disclosure, daily plant throughput is defined as the number of barrels of fresh

feed boiling above about 650° F which that plant processes per average day of operation to liquid products boiling below about 430° F. For example, in one commercially successful type of FCC-VGO operation, about 8 to about 12 tons of catalyst are under circulation in the process per 1000 barrels per day of plant through-

put. In another commercially successful process, this ratio is in the range of about 2 to 3. While the present invention may be practiced in the range of about 2 to about 30 and more typically about 2 to about 12 tons of catalyst inventory per 1000 barrels of daily plant throughput, it is preferred to carry out the process of

the present invention with a very small ratio of catalyst weight to daily plant throughput. More specifically it is preferred to carry out the process of the present invention with an inventory of catalyst that is sufficient to contact the feed for the desired residence time in the above indicated catalyst to oil ratio while minimizing

the amount of catalyst inventory relative to plant throughput, which is undergoing circulation or being held for treatment in other phases of the process such as, for example, stripping, regeneration and the like. Thus, more particularly it is preferred to carry out the process of the present invention with about 2 to about 5

In the practice of the invention, catalyst may be added continuously or periodically such as, for example, to make up for normal losses of catalyst from the system. Moreover catalyst addition may be conducted

In conjunction with withdrawal of catalyst, such as, for example, to maintain or increase the average activity level of the catalyst in the unit. For example, the rate at which virgin catalyst is added to the unit may be in the range of about 0.1 to about 3, more preferably about 0.15 to about 2, and most preferably to about 0.2 to about 1.5 pounds per barrel of feed. From the other hand

about 1.5 pounds per barrel of feed. If on the other hand equilibrium catalyst from FCC operation is to be utilized, replacement rates as high as about 5 pounds per barrel can be practiced. Where circumstances are such that the catalyst employed in the unit is below average in resistance to deactivation and/or conditions prevailing in the unit are such as to promote more rapid deactivation, replacement rates may be increased.

ing in the salt re such as to promote more rapid denaturation, one may employ rates of addition greater than those stated above; but in the opposite circumstances, lower rates of addition may be employed. By way of illustration, if a test were operated with a metal(s) loading of 5000 ppm Ni+V in parts by weight on equilibrium catalyst, one might for example employ a replace-

tion catalysts, one might, for example, employ a replacement rate of about 2.7 pounds of catalyst introduced for each barrel (42 gallons) of feed processed. However, operation at a higher level such as 10,000 ppm Ni + V on catalyst would enable one to substantially reduce the replacement rate, such as for example to about 1.3 pounds of catalyst per barrel of feed. Thus, the levels of

points on catalyst per carrier or atom. Also, the values of metal(s) on catalyst and catalyst replacement rates may in general be respectively increased and decreased to any value consistent with the catalyst activity which is available and desired for conducting the process.

Without wishing to be bound by any theory it appears that a number of features of the process to be

described in greater detail below such as, for instance,

the residence time and optimal loading of steam with the feedstock, tend to restrict the extent to which cracking conditions produce metals in the reduced state of the catalyst from heavy metal sulfides, sulfates or oxides deposited on the catalyst particles by prior exposure to carbon-metal feedstocks and regeneration conditions. Thus, the process appears to afford significant control over the deleterious effect of heavy metals on the catalyst even when the accumulations of such metals are quite substantial.

Accordingly, the process may be practiced with catalyst bearing accumulations of heavy metal(s) in the form of elemental metal(s), oxide(s), sulfide(s) or other compounds which heretofore would have been considered quite intolerable in conventional CC-VGO operations. Thus, operation of the process with catalyst bearing heavy metal accumulations in the range of about 1,500 or more ppm Equivalent Nickel, on the average, is contemplated. The concentration of Equivalent Nickel metals on catalyst can range up to about 6,000 ppm. More preferably the accumulations may be in the range of about 1,500 to about 4,000 ppm, or about 2,800 to about 4,200 ppm. The foregoing ranges are based on parts per million of Equivalent Nickel, in which the metals are expressed as metal, by weight, measured on and based on regenerated equilibrium catalyst.

In any event, the equilibrium concentrations of heavy metals in the circulating inventory of catalyst can be controlled (including maintained or varied as desired or needed) by manipulation of the rate of catalyst addition or discharge above. Thus, for example, addition of catalyst may be maintained at a rate which will control the heavy metal accumulation on the catalyst in one of the ranges set forth above. Alternatively, the relative quantities of gas oil feed and carbon-metal(s) oil feed may be varied as well as the catalyst to oil weight ratio employed in the cracking reaction.

In general, it is preferred to employ a catalyst having a relatively high level of cracking activity providing high levels of conversion and productivity at low residence times. The conversion capabilities of the catalyst may be expressed in terms of the conversion produced during actual operation of the process and/or in terms of conversion produced in standard catalyst activity tests. For example, it is preferred to employ catalyst which, in the course of extended operation under prevailing process conditions, is sufficiently active for sustaining a level of conversion of at least about 50% and more preferably at least about 60%. In this connection, conversion is expressed in liquid volume percent, based on fresh feed.

Also, for example, the preferred catalyst may be defined as one which, in its virgin or equilibrium state, exhibits a specified activity expressed as a percentage in terms of MAT (macro-activity test) conversion. For purposes of the present invention the foregoing percentage is the volume percentage of standard feedstock which a catalyst under evaluation will convert to 430° F. 16 WHSV (weight hourly space velocity calculated on a moisture free basis, using close catalyst which has been dried at 1100° F. weighted and then conditioned, for period of at least 8 hours at about 23° C and 50% relative humidity until about one hour or less prior to commencing the feed) and 100% (catalyst to oil weight ratio) by ASTM D-32 MAT test D-3907-80, using an appropriate standard feedstock, e.g. a sweet light primary gas oil, such as that used by Davison, Division of

W. R. Grace, having the following analysis and properties.

API Gravity at 60° F., degrees	31.2
Specific Gravity at 60° F., g/cc	0.8798
Residual Carbon, wt. %	0.59
Carbonaceous Carbon, wt. % (calc.)	0.2
Carbon, wt. %	0.45
Hydrogen, wt. %	12.84
Chlorine, wt. %	0.03
Nitrogen, ppm	385
Viscosity at 100° F. centistokes	10.34
Viscosity at 150° F. centistokes	11.10
Asphalt Pene	112
Penetration, Pen. %	11.7
Chlorine, Vol. %	1.4
Hydrogen, Vol. %	12.7
Aromaticity, Vol. %	24
Average Molecular Weight	264
Moist	Trace
Vanadium	Trace
Iron	Trace
Sulfur	Trace
Chlorides	Trace
S & W	Trace
Distillation	ASTM D-1160
Dist	443
10%	601
20%	654
40%	701
60%	724
80%	737
90%	744

The gasoline and diesel and boiling temperature-volume percent relationships of the product produced by the MAT conversion test may for example be determined by simulated distillation techniques, for example modifications of gas chromatographic "Sim-D" ASTM D-2887-75. The results of such simulations are in reasonable agreement with the results obtained by subjecting larger samples of material to standard laboratory distillation techniques. Conversion is calculated by subtracting from 100 the volume percent (based on fresh feed) of those products heavier than gasoline which remain in the recovered product.

On pages 525-537 of Hoggins and Watson, *Chemical Process Principles* John Wiley & Sons, Inc. N.Y. (1947), the concept of "Activity Factor" is discussed. This concept leads to the use of "relative activity" to compare the effectiveness of an operating catalyst against a standard catalyst. Relative activity measurements facilitate recognition of how the quantity requirements of various catalysts differ from one another. Thus, relative activity is a ratio obtained by dividing the weight of a standard or reference catalyst which is or would be required to produce a given level of conversion, as compared to the weight of an operating catalyst (whether proposed or actually used) which is or would be required to produce the same level of conversion in the same or equivalent feedstock under the same or equivalent conditions. Said ratio of catalyst weights may be expressed as a numerical ratio, but preferably is converted to a percentage basis. The standard catalyst is preferably chosen from among catalysts useful for conducting the present invention, such as for example zeolite fluid cracking catalysts, and is chosen for its ability to produce a predetermined level of conversion in a standard feed under the conditions of temperature, WHSV, catalyst to oil ratio and other conditions set forth in the preceding description of the MAT conver-

sion test and as ASTM D-32 MAT test D-3907-80. Conversion is the volume percentage of feedstock that is converted to 430° F. end-point gasoline, lighter products and coke. For standard feed, one may employ the above-mentioned light primary gas oil, or equivalent.

For purposes of conducting relative activity determinations, one may prepare a "standard catalyst curve" a chart or graph of conversion (as above defined) vs. reciprocal WHSV for the standard catalyst and feedstock. A sufficient number of runs is made under ASTM D-3907-80 conditions (as modified above) using standard feedstock at varying levels of WHSV to prepare an accurate "curve" of conversion vs. WHSV for the standard feedstock. This curve should traverse all or substantially all of the various levels of conversion including the range of conversion within which it is expected that the operating catalyst will be tested. From this curve, one may establish a standard WHSV for test comparison and a standard value of reciprocal WHSV corresponding to that level of conversion which has been chosen to represent 100% relative activity in the standard catalyst. For purposes of the present disclosure the aforementioned reciprocal WHSV and level of conversion are, respectively 0.0025 and 15%. In making an operating catalyst of unknown relative activity one conducts a sufficient number of runs with that catalyst under D-3907-80 conditions (as modified above) to establish the level of conversion which is or would be produced with the operating catalyst at standard reciprocal WHSV. Then, using the above-mentioned standard catalyst curve, one establishes a hypothetical reciprocal WHSV constituting the reciprocal WHSV which would have been required, using the standard catalyst, to obtain the same level of conversion which was or would be exhibited, by the operating catalyst at standard WHSV. The relative activity may then be calculated by dividing the hypothetical reciprocal WHSV by the reciprocal standard WHSV which is 1/16, or 0.0625. The result is relative activity expressed in terms of a decimal fraction, which may then be multiplied by 100 to convert to percent relative activity. In applying the results of this determination, a relative activity of 0.5, or 50%, means that it would take twice the amount of the operating catalyst to give the same conversion as the standard catalyst, i.e. the production catalyst is 50% as active as the reference catalyst.

The catalyst may be introduced into the process in its virgin form or as previously indicated, in other than virgin form, e.g. one may use equilibrium catalyst withdrawn from another test, such as catalyst that has been employed in the cracking of a different feed. Whether characterized on the basis of MAT conversion activity or relative activity, the preferred catalyst may be described as the basis of their activity "as introduced" into the process of the present invention, or on the basis of their "as withdrawn" or equilibrium activity in the process of the present invention, or on both of those bases. A preferred activity level of virgin and non-virgin catalyst "as introduced" into the process of the present invention is at least about 60% by MAT conversion, and preferably at least about 20%, more preferably at least about 40% and still more preferably at least about 60% in terms of relative activity. However, it will be appreciated that, particularly in the case of non-virgin catalysts supplied at high addition rates, lower activity levels may be acceptable. An acceptable "as withdrawn" or equilibrium activity level of catalyst which has been used in the process of the present invention is

at least about 20% or more, but about 40% or more and preferably about 60% or more are preferred values on a relative activity basis, and its activity level of 60% or more on a MAT conversion basis is also contemplated. More preferably it is desired to employ a catalyst which will, under the conditions of use in the unit, establish an equilibrium activity at or above the indicated level. The catalyst activities are determined with catalyst having less than 0.01 coke, e.g. regenerated catalyst.

One may employ any hydrocarbon cracking catalyst having the above indicated conversion capabilities. A particularly preferred class of catalyst includes those which have pore structures into which molecules of feed material may enter for adsorption and/or for contact with active catalyst sites within or adjacent the pores. Various types of catalysts are available within the classification, including for example the layered silicates, e.g. zeolites. Although the most widely available catalysts within this classification are the well-known zeolite-containing catalysts, non-zeolite catalysts are also contemplated.

The preferred zeolite-containing catalysts may include any zeolite, whether natural, semi-synthetic or synthetic, alone or in admixture with other materials which do not significantly impair the stability of the catalyst, provided the resultant catalyst has the activity and pore structure referred to above. For example, if the virgin catalyst is zeolite, it may include the zeolite component associated with or dispersed in a porous refractory inorganic oxide carrier. In such case the catalyst may for example contain about 1% to about 60%, more preferably about 15 to about 30%, and most typically about 30 to about 45% by weight, based on the total weight of catalyst (water free basis) of the zeolite, the balance of the catalyst being the porous refractory inorganic oxide alone or in combination with any of the known adjuvants for processing or improving zeolite desired and undesired reactions. For a general explanation of the nature of zeolite, molecular sieve catalysts used in the invention, attention is drawn to the disclosures of the articles entitled "Zeolite Catalysts Are a Fluid Bed" and "Making Cat Crackers Work On Varied Dies" appearing respectively in the July 26, 1978 and Sept. 11, 1978 issues of Chemical Week magazine. The disclosures of the aforementioned publications are incorporated herein by reference.

For the most part, the zeolite components of the zeolite-containing catalysts will be those which are known to be useful in FCC cracking processes. In general, these are crystalline aluminosilicates, typically made up of tetra coordinated aluminum atoms associated through oxygen atoms with adjacent silicon atoms in the crystal structure. However, the term "zeolite" as used in this disclosure encompasses not only aluminosilicates, but also substances in which the aluminum has been partly or wholly replaced, such as for instance by gallium and/or other metal atoms, and further includes substances in which all or part of the silicon has been replaced, such as for instance by germanium. Zeolite and zeolite substitution may also be practiced.

Most zeolites are prepared or occur naturally in the sodium form, so that sodium cations are associated with the electro-negative sites in the crystal structure. The sodium cations tend to make zeolites sensitive and much less stable when exposed to hydrocarbon conversion conditions, particularly high temperatures. Accordingly the zeolite may be ion exchanged, and where the

zeolite is a component of a catalyst composition, such as the zeolite may occur before or after incorporation of the zeolite as a component of the composition. Suitable catalysts for replacement of sodium in the zeolite crystal structure include ammonium (decomposable to hydrogen), hydrogen, rare earth metals, alkaline earth metals, etc. Various suitable ion exchange process can and cannot which may be exchanged into the zeolite crystal structure are well known to those skilled in the art.

Examples of the naturally occurring crystalline aluminosilicate zeolites which may be used as or included in the catalyst for the present invention are faujasite, mordenite, clinoptilolite, chabazite, zeolite, erionite, as well as levalite, heulandite, pentolite, zeolite, faujasite, heulandite, zeolite, stibite, harmotome, phillipsite, brewsterite, thulite, datolite, melilite, cancrinite, leucite, hewettite, apophyllite, natrolite, nepheline, analcime, gismondine and so forth.

Examples of the synthetic crystalline aluminosilicate zeolites which are useful as or in the catalyst for carrying out the present invention are Zeolite X, U.S. Pat. No. 2,622,444; Zeolite Y, U.S. Pat. No. 3,110,007; and Zeolite A, U.S. Pat. No. 3,082,583; as well as Zeolite B, U.S. Pat. No. 3,028,801; Zeolite D, Canada patent No. 661,581; Zeolite E, Canada patent No. 614,495; Zeolite F, U.S. Pat. No. 3,042,124; Zeolite G, U.S. Pat. No. 3,010,799; Zeolite H, U.S. Pat. No. 3,011,649; Zeolite I, Canada patent No. 575,177; Zeolite M, U.S. Pat. No. 3,095,451; Zeolite O, U.S. Pat. No. 3,140,232; Zeolite Q, U.S. Pat. No. 2,991,151; Zeolite S, U.S. Pat. No. 3,034,457; Zeolite T, U.S. Pat. No. 3,050,971; Zeolite W, U.S. Pat. No. 3,012,833; Zeolite Z, Canada patent No. 614,495; Zeolite ZK-4H, alpha beta and ZSM-type zeolites are useful. Moreover the zeolites described in U.S. Pat. Nos. 3,140,249; 3,140,251; 3,044,442 and 4,137,151 are also useful, the disclosures of said patents being incorporated herein by reference.

The crystalline aluminosilicate zeolites having a framework-type crystal structure are particularly preferred for use in the present invention. This includes particularly natural faujasite and Zeolite X and Zeolite Y.

The crystalline aluminosilicate zeolites, such as synthetic faujasite, will under normal conditions crystallize as regularly shaped, discrete particles of about one to about ten microns in size, and, accordingly this is the size range frequently found in commercial catalysts which can be used in the invention. Preferably the particle size of the zeolite is from about 0.1 to about 10 microns and more preferably is from about 0.1 to about 2 microns or less. For example, zeolites prepared in situ from external hosts may be characterized by even smaller crystallites. Crystalline zeolites exhibit both an interior and an exterior surface area, which we have defined as "total surface area", with the largest portion of the total surface area being internal. By partial surface area, we refer to the outer surface of the zeolite crystal through which reactants are considered to pass in order to convert to lower boiling products. Blockages of the internal channels by, for example, coke formation, blockages of entrance to the internal channels by deposition of coke on the partial surface area, and contamination by metals poisoning, will greatly reduce the total surface area. Therefore, to maintain the effect of contamination and pore blockage, crystals

larger than the normal size cited above are preferably not used in the catalyst of this invention.

Commercial zeolite-containing catalysts are available with carriers containing a variety of metal oxides and combinations thereof including for example alumina, silica, magnesia, and mixtures thereof and mixtures of such oxides with clays as e.g. described in U.S. Pat. No. 3,034,948. One may for example select any of the zeolite-containing molecular sieve fluid cracking catalysts which are suitable for production of gasoline from vacuum gas oils. However certain advantages may be attained by judicious selection of catalysts having marked resistance to metals. A metal resistant zeolite catalyst is, for instance, described in U.S. Pat. No. 3,944,442, in which the catalyst contains 1-40 weight percent of a rare earth-exchanged zeolite, the balance being a refractory metal oxide having specified pore volume and size distribution. Other catalysts described as "metal-tolerant" are described in the above mentioned Chabale et al. article.

In general, it is preferred to employ catalysts having an overall particle size in the range of about 5 to about 160 microns, preferably about 40 to about 120, and more preferably about 40 to about 80 microns. For example, a useful catalyst may have a skeletal density of about 150 pounds per cubic foot and an average particle size of about 50-100 microns, with one size 100 microns or less having a size less than about 40 microns and less than 80% having size less than about 50-60 microns.

Although a wide variety of other catalysts, including both zeolite-containing and non-zeolite-containing may be employed in the practice of the invention the following are examples of commercially available catalysts which may be employed in practicing the invention.

TABLE 2

	Skeletal Density					
	SiO ₂	Al ₂ O ₃	SiO ₂	SiO ₂	SiO ₂	SiO ₂
AGZ-200	800	11.0	20.7	20.0	0.40	0.11
GRZ-1	162	14.0	11.4	6.0	0.10	0.4
CCZ-220	130	11.0	14.0	6.0	0.40	0.57
Super DX	155	13.0	71.0	66.0	0.80	0.57
P-47	240	30.0	64.0	35.0	0.30	0.30
FOC-90	180	1.0	44.0	35.0	0.65	0.65
HFZ-35	110	36.0	39.0	60.0	0.47	0.54
HBZ-35	110	36.0	39.0	35.0	0.40	0.40

The AGZ-200, GRZ-1, CCZ-220 and Super DX catalysts referred to above are products of W. H. Grace and Co. F-47 and FOC-90 are products of Filtrol while HFZ-35 and HBZ-35 are products of Engelhard-Fluorid. The above are properties of virgin catalysts and, except in the case of zeolite content, are adjusted to a water free basis, i.e. based on material ignited at 1750° F. The zeolite content is derived by comparison of the X-ray intensities of a catalyst sample and of a standard material composed of high purity sodium Y zeolite in accordance with draft #6, dated Jan. 9, 1978, of proposed ASTM Standard Method entitled "Determination of the Faujasite Content of Catalyst".

Among the above mentioned commercially available catalysts, the Super D family and especially a catalyst designated GRZ-1 are particularly preferred. For example, Super DX has given particularly good results with Amstar light crudes. The GRZ-1 although sub-

stantially more expensive than the Super DX at present, appears nevertheless more advantageous.

Although not yet commercially available, it is believed that the best catalyst for carrying out the present invention will be those which, according to proposals advanced by Dr. William P. Hettenger, Jr. and Dr. James R. Lewis, are characterized by zeolites with smaller pores having large entrance diameters and large mouths to facilitate diffusion of high molecular weight molecules through the matrix to the partial surface area of zeolite active particles within the matrix. Such matrices preferably also have a relatively large pore volume in order to seek up unimpeded portions of the (carbonaceous) oil feed. Thus significant numbers of liquid hydrocarbon molecules can diffuse to active catalytic sites both in the matrix and in zeolite particles on the surface of the matrix. In general, it is preferred to employ catalysts with matrices wherein the feeder pores have diameters in the range of about 400 to about 6000, angstrom units, and preferably about 1000 to about 6000 angstrom units.

It is considered an advantage that the process of the present invention can be conducted in the substantial absence of the sulfur atmosphere or at least in the presence of a catalyst which is substantially free of either or both of these agents.

Accordingly to a particularly preferred embodiment, the catalyst comprises a Vanadium trap as disclosed in a U.S. Pat. No. 4,443,184 entitled "Trapping of Metals Deposited on Catalysts Materials During Carbon-Metal". In Oil Conversion filed in the U.S. Patent and Trademark Office on Apr. 10, 1981 in the name of William P. Hettenger, Jr. et al., the entire disclosure of which is hereby incorporated by reference. It is also preferred to employ catalysts having metal additives as described in PCT International Application Serial No. PCT/US81/00346, filed in the U.S. Patenting Office on Mar. 19, 1981 in the name of Ashland Oil, Inc., et al., entitled "Control of Vanadia Deposited on Catalyst Materials During Carbon-Metal".

The process of the present invention may be operated with the gas oil feed, carbon-metal oil feed and catalyst as substantially the sole materials charged to the reaction zone. But the charging of additional materials is not excluded. The charging of recycled oil to the reaction zone has already been mentioned. As described in greater detail below all other materials filling a variety of functions may also be charged. In such case, gas oil, carbon-metal oil and catalyst usually represent the major proportion by weight of the total of all materials charged to the reaction zone.

Certain of the additional materials which may be used perform functions which offer significant advantages over the process as performed with only gas oil, carbon-metal oil and catalyst. Among these functions are: controlling the effects of heavy metals and other catalyst contaminants; enhancing catalyst activity; absorbing some heat in the catalyst as received from the regenerator; disposal of pollutants or conversion thereof to a form or forms in which they may be more readily separated from products and/or disposed of; controlling catalyst temperature; diluting gas oil and carbon-metal oil vapors to reduce their partial pressure and increase the yield of desired products; adjusting feed/catalyst contact time; densification of hydrogen as a

hydrogen deficient carbon-metal oil feedstock, for example as disclosed in a U.S. patent application Ser. No. 246,791, now U.S. Pat. No. 4,378,034, entitled "Use of Hydrogen in Carbon-Metal Oil Conversion" and filed in the name of George D. Myers on Mar. 23, 1981 existing in the possession of the feed and possibly also distillation of products. Certain of the metals in the heavy metal accumulation on the catalyst are more active in promoting undesired reactions when they are in the form of elemental metal, than they are when in the oxidized form produced by contact with oxygen in the catalyst regenerator. However the use of contact between catalyst and vapors of feed and product in just conventional catalytic cracking was sufficient so that hydrogen released in the cracking reaction was able to react with a significant portion of the less harmful oxides back to the more harmful elemental heavy metals. One can take advantage of this situation through the introduction of additional materials which are in gaseous (including vaporous) form in the reaction zone in admixture with the catalyst and vapors of feed and product. The increased volume of material in the reaction zone resulting from the presence of such additional materials tends to increase the velocity of flow through the reaction zone with a corresponding decrease in the residence time of the catalyst and oxidized heavy metals borne thereby. Because of this reduced residence time, there is less opportunity for reduction of the oxidized heavy metals to elemental form and therefore less of the harmful elemental metals are available for forming the feed and product.

Additional materials may be introduced into the process in any suitable fashion, even examples of which follow. For instance, they may be introduced with the oil feedstock prior to contact of the latter with the catalyst. Alternatively the added materials may, if desired, be introduced with the catalyst prior to contact of the latter with the feedstock. Separate portions of the added materials may be separately introduced with both catalyst and feed materials. Moreover, the feedstock, catalyst and additional materials may, if desired, be brought together substantially simultaneously. A portion of the added materials may be mixed with catalyst and/or feed material in any of the above described ways, while additional portions are subsequently brought into admixture. For example, a portion of the added materials may be added to the feed material and/or to the catalyst before they reach the reaction zone, while another portion of the added materials is introduced directly into the reaction zone. The added materials may be introduced at a plurality of spaced locations in the reaction zone or along the length thereof if elongated.

The amount of additional materials which may be present in the feed, catalyst or reaction zone for carrying out the above functions, and others, may be varied as desired, but said amount will preferably be sufficient to substantially limit the process. These materials may for example be introduced into the reaction zone in a weight ratio relative to feed of up to about 0.4, preferably in the range of about 0.03 to about 0.4, more preferably about 0.03 to about 0.1 and most preferably about 0.03 to about 0.05.

For example, many or all of the above desirable functions may be attained by introducing H₂O to the reaction zone in the form of steam or of liquid water or a combination thereof in a weight ratio relative to feed in the range of about 0.04 or more, or even preferably about 0.05 to about 0.1 or more. Without wishing to be

based by any theory it appears that the use of H₂O tends to inhibit reduction of catalyst-borne oxides, sulfides and sulfates to the free metallic form which is believed to promote condensation-dehydrogenation with consequent promotion of coke and hydrogen yield and accompanying loss of product. Moreover H₂O may also, in some extent, reduce deposition of metals onto the catalyst surface. There may also be some tendency to desorb nitrogen-containing and other heavy condensation-containing molecules from the surface of the catalyst particles, or at least some tendency to inhibit their absorption by the catalyst. It is also believed that added H₂O tends to increase the solubility of the catalyst by Brønsted acid formation which in turn enhances the activity of the catalyst. Assuming the H₂O as supplied is cooler than the regenerated catalyst and/or the temperature of the reaction zone, the available heat involved in raising the temperature of the H₂O upon contacting the catalyst in the reaction zone or elsewhere can absorb excess heat from the catalyst. Where the H₂O is or includes recycled water that contains for example about 500 to about 5000 ppm of H₂ dissolved therein, a number of additional advantages may accrue. The ecologically unattractive H₂S need not be vented to the atmosphere, the recycled water does not require further treatment to remove H₂S and the H₂S may be of assistance in reducing coking of the catalyst by passivation of the heavy metals, i.e. by conversion thereof to the sulfide form which has a lesser tendency than the free metals to enhance coke and hydrogen production. It is the reaction zone, the presence of H₂O can dilute the carbon-metallic oil vapors, thus reducing their partial pressure and tending to increase the yield of the desired products. It has been reported that H₂O is useful in combination with other materials in generating hydrogen during cracking; thus it may be able to act as a hydrogen donor for hydrogen deficient carbon-metallic oil feedstocks. The H₂O may also serve certain purely mechanical functions such as assisting in the atomizing or dispersion of the feed, competing with high molecular weight molecules for adsorption on the surface of the catalyst, thus interrupting coke formation, steam distillation of vaporizable product from unvaporized feed material, and disengagement of product from catalyst upon completion of the cracking reaction. It is particularly preferred to bring together H₂O, catalyst and feed material substantially simultaneously. For example, one may inject H₂O and feedstock in an atomizing nozzle and immediately direct the resultant spray into contact with the catalyst at the downstream end of the reaction zone.

The addition of steam to the reaction zone is frequently mentioned in the literature of fluid catalyst cracking. Addition of liquid water to the feed is discussed relatively infrequently compared to the introduction of steam directly into the reaction zone. However, in accordance with the present invention it is particularly preferred that liquid water be brought into intimate admixture with the feed material in a weight ratio of about 0.04 to about 0.25 at or prior to the time of introduction of the oil into the reaction zone, whereby the water (e.g., in the form of liquid water or in the form of steam produced by vaporization of liquid water in contact with the oil) enters the reaction zone as part of the flow of feedstock which enters such zone. Although not wishing to be bound by any theory it is believed that the foregoing is advantageous in promoting dispersion of the feedstock. Also, the heat of vapor-

ization of the water which has been absorbed from the catalyst, from the feedstock, or from both, causes the water to be a more efficient heat sink than steam alone. Preferably the weight ratio of liquid water to feed is about 0.04 to about 0.25 more preferably about 0.05 to about 0.15.

Of course, the liquid water may be introduced into the process in the above described manner or in other ways, and in either event the introduction of liquid water may be accompanied by the introduction of additional amounts of water as steam into the zone or different portions of the reaction zone or into the catalyst and/or feedstock. For example, the amount of additional steam may be in a weight ratio relative to feed in the range of about 0.01 to about 0.25, with the weight ratio of total H₂O (as steam and liquid water) to feedstock being about 0.3 or less. The charging weight ratio of liquid water relative to steam in such combined use of liquid water and steam may for example range from about 15 which is presently preferred, to about 0.2. Such ratio may be maintained at a predetermined level within such range or varied as necessary or desired to adjust or maintain heat balance.

Other materials may be added to the reaction zone to perform one or more of the above described functions. For example, the dehydrogenation-condensation activity of γ -waxes may be inhibited by introducing hydrogen sulfide gas into the reaction zone. Hydrogen may be made available for hydrogen deficient carbon-metallic oil feedstocks by atomizing into the reaction zone either a conventional hydrogen donor diluent such as a heavy naphtha or relatively low molecular weight carbon-hydrogen fragment comprising, for example, light paraffins, low molecular weight alcohols and other compounds which permit or favor intermolecular hydrogen transfer and compounds that chemically combine to generate hydrogen in the reaction zone such as by reaction of carbon monoxide with water or with alcohols, or with olefins, or with other materials or mixtures of the foregoing.

All of the above mentioned additional materials (including water), alone or in combination with each other or in combination with other materials, such as nitrogen or other inert gases, light hydrocarbons, and others, may perform any of the above-described functions for which they are suitable, including without limitation, acting as diluents to reduce feed partial pressure and/or as heat sinks to absorb excess heat present in the catalyst as received from the regeneration step. The foregoing is a discussion of some of the functions which can be performed by materials other than the catalyst and feedstock when they are introduced into the reaction zone, and it should be understood that other materials may be added or other functions performed without departing from the spirit of the invention.

The invention may be practiced in a wide variety of apparatus. However, the preferred apparatus includes means for rapidly separating as much feed as possible and efficiently admitting feed and catalyst (although not necessarily in that order), for creating the resultant mixture to flow in a dilute suspension in a progressive flow mode, and for separating the catalyst from cracked products and any uncracked or only partially cracked feed at the end of a predetermined residence time or more, it being preferred that all or at least a substantial portion of the product should be sharply separated from at least a portion of the catalyst.

For example, the apparatus may include, along its elongated reaction chamber one or more points for introduction of catalyst-specific feed, one or more points for introduction of catalyst, one or more points for introduction of additional material, one or more points for withdrawal of products and one or more points for withdrawal of catalyst. The means for introducing feed, catalyst and other material may range from open pipes to sophisticated jets or spray nozzles, it being preferred to use means capable of breaking up the liquid feed into fine droplets. According to a particularly preferred embodiment based on a suggestion which is understood to have emanated from Mr. Steven M. Kovach, the liquid water and carbon-metallic oil, prior to their introduction into the reactor are caused to pass through a propeller operated disk, or any appropriate high shear agitating means for forming a "homogenized mixture" consisting of finely divided droplets of oil and/or water with air and/or steam present as a continuous phase.

It is preferred that the reaction chamber, or at least the major portion thereof, be more nearly vertical than horizontal and have a length to diameter ratio of at least about 10, more preferably about 20 or 25 or more. Use of a vertical riser type reactor is preferred. If tubular the reactor can be of uniform diameter throughout or may be provided with a continuous or step-wise increase in diameter along the reaction path to maintain or vary the velocity along the flow path.

In general, the charging means (for catalyst and feed) and the reactor configuration are such as to provide a relatively high velocity of flow and dilute suspension of catalyst. For example, the vapor or catalyst velocity in the riser will be usually at least about 15 and more typically at least about 35 feet per second. This velocity may range up to about 55 or about 75 feet or about 100 feet per second or higher. The vapor velocity at the top of the reactor may be higher than that at the bottom and may for example be about 80 feet per second at the top and about 40 feet per second at the bottom. The velocity capabilities of the reactor will be generally sufficient to prevent substantial build-up of catalyst bed in the bottom or other portion of the riser whereby the catalyst loading in the riser can be maintained below about 4 or 5 pounds, as for example 0.5 pounds, per cubic foot, respectively at the upstream (e.g. bottom) and downstream (e.g. top) ends of the riser.

The progressive flow mode involves, for example, flowing of catalyst, feed and products as a stream in a positively controlled and maintained direction established by the elongated nature of the reaction zone. This is not to suggest however that there need be strictly linear flow. As is well known, turbulent flow and "slippage" of catalyst may occur to some extent especially in certain ranges of vapor velocity and some catalyst loadings, although it has been reported advisable to employ sufficiently low catalyst loadings to restrict slippage and back-mixing.

Most preferably the reactor is one which sharply separates a substantial portion or all of the vaporized and cracked products from the catalyst as one or more points along the riser and preferably separates substantially all of the vaporized cracked products from the catalyst at the downstream end of the riser. A preferred type of reactor embodies ballistic separation of catalyst and products that is, catalyst is projected in a direction established by the riser tube, and is caused to continue in motion in the general direction so established, while

the products, having lesser momentum, are caused to make so abrupt change of direction, resulting in an abrupt, substantially instantaneous separation of product from catalyst. In a preferred embodiment referred to as a vented riser the riser tube is provided with a substantially unobstructed discharge opening at its downstream end for discharge of catalyst. An exit port in the side of the tube adjacent the downstream end receives the products. The discharge opening communicates with a catalyst flow path which extends to the usual stripper and regenerator while the exit port communicates with a product flow path which is substantially or entirely separated from the catalyst flow path and leads to separation means for separating the products from the relatively small portion of catalyst, if any which manages to gain entry to the product exit port. Examples of a ballistic separation apparatus and tank design as above described, are found in U.S. Pat. Nos. 4,066,533 and 4,070,159 to Myers et al., the disclosures of which patents are hereby incorporated herein by reference to their entirety. According to a particularly preferred embodiment, based on a suggestion understood to have emanated from Paul W. Walters, Roger M. Benkey and Dwight F. Barger the ballistic separation may include at least a partial reversal of direction by the product vapors upon discharge from the riser tube; that is, the product vapors make a turn or change of direction which exceeds 90° at the riser tube outlet. This may be accomplished for example by providing a cup-like member surrounding the riser tube at its upper end, the ratio of cross-sectional area of the cup-like member relative to the cross-sectional area of the riser tube outlet being low e.g. less than 1 and preferably less than about 0.5. Preferably the lip of the cup is slightly downstream of, or above the downstream end or top of the riser tube, and the cup is preferably concentric with the riser tube. By means of a product vapor line communicating with the interior of the cup but not the interior of the riser tube, having its inlet positioned within the cup interior in a direction upstream of the riser tube outlet, product vapors emanating from the riser tube and entering the cup by reversal of direction are transported away from the cup to catalyst and product separation equipment. Such an arrangement can produce a high degree of completion of the separation of catalyst from product vapors at the riser tube outlet, so that the required amount of auxiliary catalyst separation equipment such as cyclones is greatly reduced, with consequent large savings in capital investment and operating cost.

Preferred conditions for operation of the process are described below. Among these are feed, catalyst and reaction temperatures, reaction and feed pressures, residence time and levels of conversion, coke production and coke hydrons on catalyst.

In conventional FCC operations with VGO, the feedstock is customarily preheated, often to temperatures significantly higher than are required to make the feed sufficiently fluid for pumping and for introduction into the reactor. For example, preheat temperatures as high as about 700° or 800° F have been reported. But in our process as presently practiced it is preferred to restrict preheating of the feed, so that the feed is capable of absorbing a larger amount of heat from the catalyst while the catalyst moves the feed to conversion temperature, at the same time minimizing withdrawal of external fuels to heat the feedstock. Thus, where the nature of the feedstock permits, it may be fed at ambient temper-

ture. Heavier stocks may be fed at preheat temperatures of up to about 600° F. typically about 200° F. to about 500° F. but higher preheat temperatures are not necessarily excluded.

The catalyst fed to the reactor may vary widely in temperature, for example from about 1100° to about 1600° F. more preferably about 1200° to about 1500° F. and most preferably about 1300° to about 1400° F. with about 125 to about 1375 being considered optimum at present.

As indicated previously the conversion of the charge stock to lower molecular weight products may be conducted at a temperature of about 500° to about 600° F. measured at the reaction chamber outlet. The reaction temperature as measured at said outlet is more preferably maintained in the range of about 965 to about 1500° F. still more preferably about 975 to about 1500° F. and most preferably about 980° to about 1150° F. Depending upon the temperature selected and the properties of the feed, all of the feed may or may not vaporize in the riser.

Although the pressure in the reactor may as indicated above, range from about 10 to about 50 psia, preferred and more preferred pressure ranges are about 15 to about 35 and about 20 to about 35. In general, the partial (or total) pressure of the feed may be in the range of about 3 to about 30, more preferably about 7 to about 25 and most preferably about 10 to about 20 psia. The feed partial pressure may be controlled or suppressed by the introduction of gaseous (including vaporous) materials into the reactor such as for instance the steam, water and other additional materials described above. The process has for example been operated with the ratio of feed partial pressure relative to total pressure in the riser in the range of about 0.1 to about 0.8, more typically about 0.3 to about 0.7 and still more typically about 0.4 to about 0.6, with the ratio of added gaseous material (which may include recycled gas and/or steam resulting from absorption of H₂O to the riser in the form of steam and/or liquid water) relative to total pressure in the riser correspondingly ranging from about 0.8 to about 0.2, more typically about 0.7 to about 0.3 and still more typically about 0.6 to about 0.4. In the alternative operation just described, the ratio of the partial pressure of the added gaseous material relative to the partial pressure of the feed has been in the range of about 0.25 to about 4.0, more typically about 0.4 to about 2.5 and still more typically about 0.7 to about 1.7.

Although the residence time of feed and product vapors in the riser may be in the range of about 0.5 to about 10 seconds, as described above, preferred and more preferred values are about 0.5 to about 6 and about 1 to about 4 seconds, with about 1.5 to about 3.0 seconds currently being considered about optimum. For example, the process has been operated with a riser vapor residence time of about 2.5 seconds or less by introduction of copious amounts of gaseous materials into the riser, each amount being sufficient to provide for example a partial pressure ratio of added gaseous materials relative to hydrocarbon feed of about 0.8 or more. By way of further illustration, the process has been operated with said residence time being about two seconds or less, with the aforementioned ratio being in the range of about 1 to about 3. The combination of low feed partial pressure, very low residence time and facile separation of product from catalyst are considered especially beneficial for the conversion of carbometallic oils. Additional benefits may be obtained in the fore-

going combination when there is a substantial partial pressure of added gaseous material, especially H₂O as described above.

Depending upon whether there is a bypass between the catalyst and hydrocarbon vapors in the riser, the catalyst riser residence time may or may not be the same as that of the vapors. Thus, the ratio of average catalyst riser residence time versus vapor riser residence time, i.e., slippage, may be in the range of about 1 to about 3 more preferably about 1 to about 4 and most preferably about 1 to about 3 with about 1 to about 2 currently being considered optimum.

In practice, there will usually be a small amount of slippage, e.g., at least about 1.05 or 1.2. In an operating unit there may for example be a slippage of about 1.1 at the bottom of the riser and about 1.05 at the top.

In certain types of known FCC units, there is a riser which discharges catalyst and product vapors together into an enlarged chamber usually considered to be part of the reactor in which the catalyst is discharged from product and collected. Confined contact of catalyst, uncracked feed (if any) and cracked products in such enlarged chamber results in an overall catalyst feed contact time appreciably exceeding the riser tube residence times of the vapors and catalyst. When practicing the process of the present invention with intimate contact of catalyst and vapors at the downstream (e.g., upper) extremity of the riser, such as is taught in the above mentioned Myers et al. patents, the riser residence time and vapor catalyst contact time are substantially the same for a major portion of the feed and product vapors. It is considered advantageous if the vapor riser residence time and vapor catalyst contact time are substantially at least about 80% and most preferably at least about 90% and most preferably at least about 95% by volume of the total feed and product vapors passing through the riser. By denying such vapors confined contact with catalyst in a catalyst discharge and collection chamber one may avoid a tendency toward re-cracking and diminished selectivity.

In general, the combination of catalyst to oil ratio, temperature, pressure and residence time should be such as to effect a substantial conversion of the mixture of feedstocks. It is an advantage of the process that very high levels of conversion can be attained in a single pass, for example the conversion may be in excess of 50% and may range to about 90% or higher. Preferably the aforementioned conditions are maintained at levels sufficient to maintain conversion levels in the range of about 60 to about 90% and more preferably about 70 to about 85%. The foregoing conversion levels are calculated by subtracting from 100% the percentage obtained by dividing the liquid volume of fresh feed into 100 times the volume of liquid product boiling at and above 430° F. (the standard atmospheric pressure).

These substantial levels of conversion may and usually do result in relatively large yields of coke, such as for example about 4 to about 14% by weight based on fresh feed, more commonly about 6 to about 13% and most frequently about 10 to about 13%. The coke yield can more or less quantitatively deposit upon the catalyst. At contemplated catalyst to oil ratios, the resultant coke laydown may be in excess of about 0.5 more commonly in excess of about 0.5 and very frequently in excess of about 1% of coke by weight, based on the weight of moisture free regenerated catalyst. Such coke

laydown may range as high as about 2%, or about 3%, or even higher.

In contrast with conventional FCC operations on VGO, the present process includes stripping of spent catalyst after discharge from the reactor from product vapors. Persons skilled in the art are acquainted with appropriate stripping agents and conditions for stripping spent catalyst, but in some cases the present process may require somewhat more severe conditions than are commonly employed. This may result, for example, from the use of a carbometallic oil having constituents which do not volatilize under the conditions prevailing in the reactor which constituents deposit themselves at least in part on the catalyst. Such adsorbed, unvaporized material can be troublesome from at least two standpoints. First, if the gas (including vapors) used to strip the catalyst can gain admission to a catalyst discharge or collection chamber connected to the downstream end of the riser and if there is an accumulation of catalyst in such chamber, vaporization of these unvaporized hydrocarbons in the stripper can be followed by adsorption on the bed of catalyst in the chamber. More particularly as the catalyst in the stripper is stripped of adsorbed feed material, the resultant feed material vapors pass through the bed of catalyst accumulated in the catalyst collection and/or discharge chamber and may deposit coke and/or condensed material on and around catalyst as well. As the catalyst bearing such deposits moves from the bed and into the stripper and from thence to the regenerator the condensed products can create a demand for more stripping capacity while the coke can tend to increase regeneration temperatures and/or demand greater regeneration capacity. For the foregoing reasons, it is preferred to prevent or restrict contact between stripping vapors and catalyst accumulations in the catalyst discharge or collection chamber. This may be done for example by preventing such accumulations from forming, e.g., with the exception of a quantity of catalyst which essentially drops out of circulation and may remain at the bottom of the discharge and/or collection chamber the catalyst that is in circulation may be removed from said chamber promptly upon settling to the bottom of the chamber. Also, to enhance regeneration temperatures and demand for regeneration capacity it may be desirable to employ conditions of time, temperature and atmosphere in the stripper which are sufficient to reduce potentially volatile hydrocarbon material borne by the stripped catalyst to about 10% or less by weight of the total carbon loading on the catalyst. Such stripping may for example include releasing of the catalyst, extensive stripping with steam, the use of gases having a temperature considered higher than normal for FCC/VGO operations, such as for instance flue gas from the regenerator as well as other refinery stream gas such as hydrocarbon off-gas (H₂S containing), hydrogen and others. For example, the stripper may be operated at a temperature of about 120° F. using steam at a pressure of about 150 psig and a weight ratio of steam to catalyst of about 0.001 to about 0.003. On the other hand, the stripper may be operated at a temperature of about 1025° F. or higher.

Substantial conversion of carbometallic oils to lighter products in accordance with the invention tends to produce sufficiently large coke yields and coke laydown on catalyst to require some care in catalyst regeneration. In order to maintain adequate activity in acidic and non-acidic catalyst, it is desirable to regenerate the

catalyst under conditions of time, temperature and atmosphere sufficient to reduce the percent by weight of carbon remaining on the catalyst to about 0.25% or less, whether the catalyst bears a large heavy metals accumulation or not. Preferably this weight percentage is about 0.1% or less and more preferably about 0.05% or less, especially with molten catalysts. The amounts of coke which must therefore be burned off of the catalyst when processing carbometallic oils are usually substantially greater than would be the case when cracking VGO. The term coke when used to describe the present invention, should be understood to include any residual unvaporized feed or cracking product, if any such material is present on the catalyst after stripping.

Regeneration of catalyst, burning away of coke deposited on the catalyst during the conversion of the feed, may be performed at any suitable temperature in the range of about 1100° to about 1600° F. measured at the regenerator catalyst outlet. This temperature is preferably in the range of about 1200° to about 1500° F. more preferably about 1375° to about 1435° F. and optimally about 1325° to about 1375° F. The process has been operated, for example, with a fluidized regenerator with the temperature of the catalyst dense phase in the range of about 1300° to about 1400° F.

In accordance with the invention, regeneration may be done while maintaining the catalyst in one or more fluidized beds in one or more fluidization columns. Such fluidized bed operations are characterized, for instance, by one or more fluidized dense beds of circulating particles having a bed density of, for example, about 25 to about 50 pounds per cubic foot. Fluidization is maintained by passing gases, including combustion supporting gases, through the bed at a sufficient velocity to maintain the particles in a fluidized state but at a velocity which is sufficiently small to prevent substantial entrainment of particles in the gas. For example, the fluid velocity of the fluidizing gases may be in the range of about 0.2 to about 4 feet per second and preferably about 0.3 to about 3 feet per second. The average total residence time of the particles in the one or more beds is substantial, ranging for example from about 5 to about 30, more preferably about 5 to about 20 and still more preferably about 5 to about 10 minutes. From the foregoing, it may be readily seen that the fluidized bed regeneration of the present invention is readily distinguishable from the short-contact, low-density entrainment type regeneration which has been practiced in some FCC operations.

When regenerating catalyst to very low levels of carbon on regenerated catalyst, e.g., about 0.1% or less or about 0.05% or less, based on the weight of regenerated catalyst, it is acceptable to burn off at least about the last 10% or at least about the last 5% by weight of coke (based on the total weight of coke on the catalyst immediately prior to regeneration) to contact with combustion producing gases containing excess oxygen. In this connection it is contemplated that some selected portion of the coke, ranging from all of the coke down to about the last 5 or 10% by weight, can be burned with excess oxygen. By excess oxygen is meant an amount in excess of the stoichiometric requirement for burning all of the hydrogen, all of the carbon and all of the other combustible components, if any, which are present in the aforementioned selected portion of the coke immediately prior to regeneration. The gaseous products of combustion conducted in the presence of excess oxygen will normally include an appreciable

amount of free oxygen. Such free oxygen, unless removed from the by-product gases or converted to some other form by a means or process other than regeneration, will normally manifest itself as free oxygen in the fine gas from the regenerator unit. In order to provide sufficient driving force to complete the combustion of the coke with excess oxygen, the amount of free oxygen will usually be not merely appreciable but substantial, i.e., there will be a concentration of at least about 2 mole percent of free oxygen in the total regeneration fine gas recovered from the entire, completed regeneration operation. While such technique is effective in obtaining the desired low levels of carbon on regenerated catalyst, it has its limitations and difficulties as will become apparent from the discussion below.

Heat released by combustion of coke in the regenerator is absorbed by the catalyst and can be readily retained thereby until the regenerated catalyst is brought into contact with fresh feed. When processing carbomethane oils to the relatively high levels of conversion involved in the present invention, the amount of regenerative heat which is transmitted to fresh feed by way of recycling regenerated catalyst can substantially exceed the level of heat input which is appropriate in the riser for heating and vaporizing the feed and other materials, for supplying the endothermic heat of reaction for cracking, for making up the heat losses of the unit and so forth. Thus, in accordance with the invention, the amount of regenerator heat transmitted to fresh feed may be controlled, or estimated where necessary within certain approximate ranges. The amount of heat so transmitted may for example be in the range of about 500 to about 1200, more particularly about 600 to about 900, and more particularly about 650 to about 850 BTUs per pound of fresh feed. The aforesaid ranges refer to the combined heat, in BTUs per pound of fresh feed, which is transmitted by the catalyst to the feed and reaction products (between the contacting of feed with catalyst and the separation of product from catalyst) for supplying the heat of reaction (e.g., for cracking) and the difference in enthalpy between the products and the fresh feed. Not included in the foregoing are the heat made available in the reactor by the adsorption of coke on the catalyst, nor the heat consumed by heating, vaporizing or reacting recycle streams and such added materials as water steam ammonia and other hydrogen donors, flue gases and inert gases, or by radiation and other losses.

One or a combination of techniques may be utilized in this invention for controlling or restricting the amount of regeneration heat transmitted via catalyst to fresh feed. For example, one may add a combustion modifier to the cracking catalyst in order to reduce the temperature of combustion of coke to carbon dioxide and/or carbon monoxide in the regenerator. Moreover one may remove heat from the catalyst through heat exchange means, including for example heat exchangers (e.g., steam coils) built into the regenerator itself, whereby one may extract heat from the catalyst during regeneration. Heat exchangers can be built into catalyst transfer lines, such as for instance the catalyst return line from the regenerator to the reactor, whereby heat may be removed from the catalyst after it is regenerated. The amount of heat imparted to the catalyst in the regenerator may be restricted by reducing the amount of insulation on the regenerator to permit some heat loss to the surrounding atmosphere, especially if fluids of exceedingly high cooling potential are planned for pro-

cessing; in general, such loss of heat to the atmosphere is considered economically less desirable than certain of the other alternatives set forth herein. One may also inject cooling fluids into portions of the regenerator other than those occupied by the dense bed, for example water and/or steam, whereby the amount of inert gas available in the regenerator for heat absorption and removal is increased.

Another suitable and preferred technique for controlling or restricting the heat transmitted to fresh feed via recycled regenerated catalyst involves maintaining a specified ratio between the carbon dioxide and carbon monoxide formed in the regenerator while such gases are in heat exchange contact or relationship with catalyst undergoing regeneration. In general, all or a major portion by weight of the coke present on the catalyst immediately prior to regeneration is removed in at least one combustion zone in which the aforesaid ratio is controlled as described below. More particularly at least the major portion above preferably at least about 65% and more preferably at least about 80% by weight of the coke on the catalyst is removed in a combustion zone in which the molar ratio of CO_2 to CO is maintained at a level substantially below 5, e.g., about 4 or less. Looking at the CO_2/CO relationship from a reverse standpoint, it is preferred that the CO/CO_2 molar ratio should be at least about 0.25 and preferably at least about 0.1 and still more preferably about 0.1 or more or even 1.5 or more. While persons skilled in the art are aware of techniques for utilizing the burning of CO to CO_2 , it has been suggested that the mole ratio of CO/CO_2 should be kept less than 0.1 when regenerating catalyst with large heavy metal accumulations resulting from the processing of carbomethane oils, as this condition can for example U.S. Pat. No. 4,162,213 to Zelenak, Jr. et al. In this invention, however, CO production is increased while catalyst is regenerated to about 0.1% carbon or less, and preferably about 0.5% carbon or less. Moreover, according to a preferred method of carrying out the invention the sub-process of regeneration, as a whole, may be carried out to the above-mentioned low levels of carbon on regenerated catalyst with a deficiency of oxygen, more specifically the total oxygen supplied to the one or more stages of regeneration can be and preferably is less than the stoichiometric amount which would be required to burn all hydrogen in the coke to H_2O and to burn all carbon in the coke to CO_2 . If the coke includes other combustibles, the aforesaid stoichiometric amount can be adjusted to include the amount of oxygen required to burn them.

Still another particularly preferred technique for controlling or restricting the regeneration heat imparted to fresh feed via recycled catalyst involves the diversion of a portion of the heat borne by recycled catalyst to add materials introduced into the reactor such as the water, steam, ammonia, other hydrogen donors, flue gases, inert gases, and other gases or vaporizable materials which may be introduced into the reactor.

The larger the amount of coke which must be burned from a given weight of catalyst, the greater the potential for exposing the catalyst to excessive temperatures. Many otherwise desirable and useful cracking catalysts are particularly susceptible to deactivation at high temperatures, and among these are quite a few of the costly molecular sieve or media types of catalyst. The crystal structures of zeolites and the pore structures of the catalyst carriers generally are somewhat susceptible to

thermal and/or hydrothermal degradation. The use of such catalysts in catalytic conversion processes for carbomethane fluids creates a need for regeneration techniques which will not destroy the catalyst by exposure to highly severe temperatures and steaming. Such need can be met by a multi-stage regeneration process which includes conveying spent catalyst into a first regeneration zone and introducing oxidizing gas thereto. The amount of oxidizing gas that enters said first zone and the concentration of oxygen or oxygen bearing gas therein are sufficient for only partially effecting the desired conversion of coke on the catalyst to carbon oxide gases. The partially regenerated catalyst is then removed from the first regeneration zone and is conveyed to a second regeneration zone. Oxidizing gas is introduced into the second regeneration zone to provide a higher concentration of oxygen or oxygen-containing gas than in the first zone, to complete the removal of carbon to the desired level. The regenerated catalyst may then be removed from the second zone and recycled to the reactor for contact with fresh feed.

Multi-stage regeneration offers the possibility of controlling oxygen deficient regeneration with the control of the CO/CO_2 molar ratio. Thus, about 50% or more, more preferably about 65% to about 95%, and more preferably about 80% to about 95% by weight of the coke on the catalyst immediately prior to regeneration may be removed in one or more stages of regeneration in which the molar ratio of CO/CO_2 is controlled in the manner described above. In combination with the foregoing, the last 5% or more, or 10% or more by weight of the coke originally present, up to the entire amount of coke remaining after the preceding stage or stages, can be removed in a subsequent stage of regeneration in which more oxygen is present. Such process is susceptible of operation in such a manner that the total fine gas recovered from the entire, completed regeneration operation contains little or no excess oxygen, i.e., on the order of about 0.2 mole percent or less, or as low as about 0.1 mole percent or less, which is substantially less than the 2 mole percent which has been suggested elsewhere. Thus, multi-stage regeneration is particularly beneficial in that it provides another convenient technique for restricting regeneration heat transmitted to fresh feed via regenerated catalyst and/or reducing the potential for thermal deactivation, while simultaneously offering an opportunity to reduce the carbon level on regenerated catalyst to those very low percentages (e.g., about 0.1% or less) which particularly enhance catalyst activity. For example, a two-stage regeneration process may be carried out with the first stage burning about 60% of the coke at a bed temperature of about 1300° F. to produce CO and CO_2 in a molar ratio of CO/CO_2 of about 1 and the second stage burning about 20% of the coke at a bed temperature of about 1350° F. to produce substantially all CO_2 along with free oxygen. Use of the gases from the second stage as combustion impinging gases for the first stage, along with additional air introduced into the first stage bed, results in an overall CO to CO_2 ratio of about 0.6, with a catalyst residence time of about 5 to 15 minutes total in the two zones. Moreover, where the regeneration conditions, e.g., temperature or atmosphere, are substantially less severe in the second zone than in the first zone (e.g., by at least about 10 and preferably at least about 20° F.), that part of the regeneration sequence which involves the most severe conditions is performed while there is still an appreciable amount of coke on the cata-

lyst. Such operation may provide some protection of the catalyst from the more severe conditions. A particularly preferred embodiment of the invention is two-stage fluidized regeneration at a maximum temperature of about 1500° F. with a reduced temperature of at least about 10 or 20° F. in the dense phase of the second stage as compared to the dense phase of the first stage, and with reduction of carbon on catalyst to about 0.05% or less or even about 0.025% or less by weight in the second zone. In fact, catalyst can readily be regenerated to carbon levels as low as 0.01% by this technique, even though the carbon on catalyst prior to regeneration is as much as about 1%.

In most circumstances, it will be important to insure that no adsorbed oxygen containing gases are carried into the riser by recycled catalyst. Thus, whenever such action is considered necessary the catalyst discharged from the regenerator may be stripped with appropriate stripping gases to remove oxygen containing gases. Such stripping may for instance be conducted at relatively high temperatures, for example about 1350° to about 1370° F. using steam, nitrogen or other inert gas as the stripping gas(es). The use of nitrogen and other inert gases is beneficial from the standpoint of avoiding a tendency toward hydro-thermal catalyst destruction which may result from the use of steam.

The following comments and discussion relating to such management of carbon bearing gases are more suggestive than definitive, and are not intended to be construed as a limitation on the invention. Since these remarks are for the most part directed to what is considered the best mode of operation, it should be apparent that the invention is not limited to the particular modes of operation discussed below. Moreover, since certain of these comments are necessarily based on theoretical considerations, there is no intention to be bound by such theory, whether expressed herein or hereinafter in the operating suggestions set forth hereinafter.

Although discussed separately below it is readily apparent that metals management, carbon management and heat management are inter-related and interdependent subjects both in theory and practice. While coke yield and coke laydown on catalyst are primarily the result of the relatively large quantities of coke precursors found in carbomethane oils, the production of coke is exacerbated by high metals concentrations, which can also significantly affect catalyst performance. Moreover the degree of excess experienced in metals management and carbon management will have a direct influence on the extent to which heat management is necessary. Moreover some of the steps taken in support of metals management have proved very helpful in respect to carbon and heat management.

As noted previously the presence of a large heavy metal accumulation on the catalyst tends to aggravate the problem of dehydrogenation and aromatic condensation, resulting in increased production of gases and coke for a feedstock of a given Ramanbottom carbon value. The introduction of substantial quantities of H_2O into the reactor either in the form of steam or liquid water appears highly beneficial from the standpoint of keeping the heavy metals in a less harmful form, i.e., the oxide rather than metallic form. This is of assistance in maintaining the desired selectivity.

Also, a unit design in which system components and residence times are selected to reduce the ratio of catalyst reactor residence time relative to catalyst regenerator residence time will tend to reduce the ratio of the

times during which the catalyst is respectively under reduction conditions and oxidation conditions. This too can assist in maintaining desired levels of selectivity.

Whether the metal content of the catalyst is being managed successfully may be observed by monitoring the total hydrogen plus methane produced in the reactor and/or the ratio of hydrogen to methane thus produced. In general, it is considered that the hydrogen to methane mole ratio should be less than about 1 and preferably about 0.6 or less, with about 0.4 or less being considered about optimum. In actual practice the hydrogen to methane ratio may range from about 0.5 to about 1.5 and average about 0.8 to about 1.

Careful carbon management can improve both selectivity (the ability to manufacture products of variable products), and heat productivity. In general, the techniques of catalyst control described above are also of assistance in carbon management. The usefulness of water addition in respect to carbon management has already been spelled out in considerable detail in that part of the specification which relates to added materials for introduction into the reaction zone. In general, these techniques which improve dispersion of the feed in the reaction zone should also prove helpful, these include for instance the use of foaming or mixing devices to assist in dispersing the feed.

Catalyst to oil ratio is also a factor in heat management. In common with prior FCC practice on VGO, the reactor temperature may be controlled in the practice of the present invention by respectively increasing or decreasing the flow of hot regenerated catalyst to the reactor in response to decreases and increases in reactor temperature, typically the outlet temperature in the case of a riser type reactor. Where the automatic controller for catalyst introduction is set to maintain an excessive catalyst to oil ratio, one can expect unnecessarily large runs of carbon production and heat release, relative to the weight of fresh feed charged to the reaction zone.

Relatively high reactor temperatures are also beneficial from the standpoint of carbon management. Such higher temperatures foster more complete vaporization of feed and disengagement of product from catalyst.

Carbon management can also be facilitated by suitable restriction of the total pressure in the reactor and the partial pressure of the feed. In general, at a given level of conversion, relatively small decreases in the aforementioned pressures can substantially reduce coke production. This may be due to the fact that restricting total pressure tends to enhance vaporization of high boiling components of the feed, encourage cracking and facilitate disengagement of both unconverted feed and higher boiling cracked products from the catalyst. It may be of assistance in this regard to restrict the pressure drop of equipment downstream of and in communication with the reactor. But if it is desired or necessary to operate the system at higher total pressures, such as for instance because of operating limitations (e.g. pressure drop in downstream equipment) the above described benefits may be obtained by restricting the feed partial pressure. Suitable ranges for total reactor pressure and feed partial pressure have been set forth above, and in general it is desirable to attempt to minimize the pressure within these ranges.

The abrupt separation of catalyst from product vapors and unconverted feed (if any) is also of great assistance. It is for this reason that the so-called vented riser apparatus and technique disclosed in U.S. Pat. Nos. 4,079,159 and 4,066,533 to George D. Myers et al is the

preferred type of apparatus for conducting this process. For similar reasons, it is beneficial to reduce transfer as possible the elapsed time between separation of catalyst from product vapors and the commencement of stripping. The vented riser and prompt stripping tend to reduce the opportunity for coking of unconverted feed and higher boiling cracked products adsorbed on the catalyst.

A particularly desirable mode of operation from the standpoint of carbon management is to operate the process in the vented riser using hydrogen donor if necessary while maintaining the feed partial pressure and total reactor pressure as low as possible, and incorporating relatively large amounts of water steam and if desired, other diluents, which provide the numerous benefits discussed in greater detail above. Moreover when liquid water steam, hydrogen donors, hydrogen and other gaseous or vaporizable materials are fed to the reaction zone, the feeding of these materials provides an opportunity for exercising additional control over catalyst to oil ratio. Thus, for example, the practice of increasing or decreasing the catalyst to oil ratio for a given amount of decrease or increase in reactor temperature may be reduced or eliminated by substituting either appropriate reduction or increase in the charging ratios of the water steam and other gaseous or vaporizable material, or an appropriate reduction or increase in the ratio of water steam and/or other gaseous materials introduced into the reaction zone.

Heat management includes measures taken to control the amount of heat released in various parts of the process and/or for dealing successfully with heat as may be released. Unlike conventional FCC practice using VGO, wherein it is usually a problem to generate sufficient heat during regeneration to heat balance the reactor, the processing of carbo-metallic oils generally produces so much heat as to require careful management thereof.

Heat management can be facilitated by various techniques associated with the materials introduced into the reactor. Thus, heat absorption by feed can be maintained by extensive preheating of feed, it being necessary only that the feed temperature be high enough so that it is sufficiently fluid for successful pumping and dispersion in the reactor. When the catalyst is maintained in a highly active state with the suppression of coking (metal control), so as to achieve higher conversion, the resultant higher conversion and greater selectivity can increase the heat absorption of the reaction. In general, higher reactor temperatures promote catalyst conversion activity in the face of more refractory and higher boiling contaminants with high coking potential. While the rate of catalyst deactivation may thus be increased, the higher temperatures of operation tends to offset this loss in activity. Higher temperatures in the reactor also contribute to enhancement of coke number thus offsetting the coke depressant effect of high carbon down. Other techniques for absorbing heat have also been discussed above in connection with the introduction of water steam, and other gaseous or vaporizable materials into the reactor.

As noted above, the invention can be practiced in the above-described mode and in many others. An illustrative non-limiting example is described by the accompanying schematic diagrams in the figure and by the description of this figure which follows.

FIG 1 is a schematic diagram of an apparatus for carrying out the process of the present invention. The

feedstock (which may have been heated in a feed pre-heater not shown) and water (when used) applied through delivery pipe 9 are fed by feed supply pipe 10 having a control valve 11 to a wye 12 in which they mix with a flow of catalyst delivered through supply pipe 13 and controlled by valve 14. Of course a variety of mixing arrangements may be employed, and provisions may be made for introducing the other added materials discussed above. The mixture of catalyst and feed, with or without such additional materials, is then introduced into riser 15.

Although riser 15 appears vertical in the drawing, persons skilled in the art will recognize that the riser need not be vertical, as riser type reactors are known in which an appreciable portion of the riser pipe is non-vertical. Thus, riser pipes having an upward component of devices are contemplated, and usually the upward component of their upwardly flowing material portions is substantial, i.e. at least about 30°. It is also known to provide risers which have downwardly flowing inlets or vertical portions, as well as horizontal portions. Folded risers are also known, in which there are both upwardly extending and downwardly extending segments. Moreover it is entirely feasible to provide the process of the invention in an inclined and/or vertical pipe in which the feed and catalyst are introduced as a separate stream. In which the feed and catalyst moves under the influence of gravity and the down flow of the feed to a lower elevation. Thus, in general, the invention contemplates the use of reaction chambers having a long L/D ratio and having a significant deviation from horizontal.

At the upper end of the riser 15 is a chamber 16 which receives the catalyst from the riser. Means are provided for causing product vapors to undergo a sufficient change of direction relative to the direction traveled by the catalyst particles, whereby the vapors are suddenly and effectively separated from the catalyst. Thus, there is "instant" separation of catalyst particles and product vapors as described above.

In the present schematic diagram, the disengagement chamber 16 includes an upward extension 17 of riser pipe 15 having an open top 21 through which the catalyst particles are discharged. This embodiment makes use of the so-called vented riser described in the above-mentioned Myers et al patents. Because of the refractory nature of the feedstock fractions, relatively high severity is required, but the rapid disengagement of catalyst from lighter cracked products in the vented riser prevents overcracking of desirable liquid products such as gasoline to gaseous products. The product vapors are caused to undergo a sudden change of direction into lateral port 22 in the side of riser extension 17, the catalyst particles being, for the most part, unable to follow the product vapors into port 22.

The vapors and those few particles which do manage to follow them into port 22 are transferred by cross pipe 23 to a cyclone separator 24. It is an advantage of the vented riser system shown that it can function satisfactorily with a single stage cyclone separator. However in the present embodiment the cyclone separator 24 is employed as a first stage cyclone separator which is connected via transfer pipe 27 with optional secondary cyclone separator 25. The cyclone separator means, whether of the single- or multi-stage type, separates from the product vapors those small amounts of catalyst which do enter the lateral port 22. Product vapors are

discharged from disengagement chamber 19 through product discharge pipe 26.

The catalyst particles which discharge from open top 21 of riser pipe extension 17, and those catalyst particles which are discharged from the discharge legs 27 and 28 of primary and secondary cyclones 24 and 25 drop to the bottom of disengagement chamber 19. The inventory and residence time of catalyst in chamber 19 are preferably maintained. During startup those catalyst particles which are present may be kept in suspension by flowing jets 30 supplied with steam through steam supply pipe 29. Spent catalyst spilling over from the bottom of disengagement chamber 19 passes via drop leg 31 to a stripper chamber 22 equipped with baffles 33 and steam jet 34. Any of the other stripping gases referred to above may be employed with or in place of the steam.

Carbon is burned from the surface of the catalyst in the combustor 38 which receives stripped catalyst via downcomer pipe 39 and control valve 40. Blowers 41 and 42, in association with a valve and purging arrangement generally indicated by 44, supply air to combustion air jets 43 at the bottom of the combustor and to heating jets 49 at an elevated position. Air preheater 45, although usually named when processing heavy hydrocarbons in accordance with the invention, may be employed when starting up the unit on VGO; thus, when the unit is switched over to the gas oil and carbo-metallic feed mixture, preheater operation may be discontinued (or at least reduced). Supplemental fuel means may be provided to supply fuel through the combustor air jets 49; but such is usually unnecessary since the carbon lay down on the catalyst supplies more than enough fuel to maintain the requisite temperatures in the regeneration section. Regenerated catalyst, with most of the carbon burned off, departs the combustor through an upper outlet 50 and cross pipe 51 to a secondary chamber 52, where it is directed into the lower portion of thimbleriser by baffle 53. Although the use of two stage regeneration is contemplated, and preferred, in this particular embodiment the secondary chamber 52 was operated primarily as a separator chamber, although it can be used to remove additional carbon down to about 0.01% or less in the final stages of regeneration.

Catalyst moves in up to three different directions from the secondary chamber 52. A portion of the catalyst may be circulated back to combustor 38 via catalyst recirculation loop 55 and control valve 56 for heat control in the combustor. Some of the catalyst is entrained in the product gases, such as CO and/or CO₂ produced by burning the carbon on the catalyst in the combustor and the entrained catalyst fines pass upwardly in chamber 53 to two sets of primary and secondary cyclones generally indicated by 57 and 58 which separate these catalyst fines from the combustion gases. Catalyst collected in the cyclones 57,58 and discharged through their drop legs is directed to the bottom of chamber 52 where catalyst is kept in suspension by inert gas and/or steam jets 59 and by a baffle arrangement 64, the latter facilitating discharge of regenerated catalyst through outlet 69 to catalyst supply pipe 13 through which it is recirculated for contact with fresh feed at wye 12, as previously described.

Combustion product gases produced by regeneration of the catalyst and separated from entrained catalyst steam by the sets 57,58 of primary and secondary cyclones in chamber 52, discharge through effluent pipes

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TABLE IV-continued

Feed (Vol. %)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
CH ₄	1.1	4.5	4.1	4.3	3.3	3.9	4.1	6.3	5.0	10.6
C ₂ H ₆	7.2	6.1	5.4	5.7	5.3	5.8	7.5	8.3	8.2	
C ₃ H ₈	25.9	26.0	22.4	22.6	18.7	21.4	24.8	22.4	19.9	26.1
C ₄ -C ₁₀ F	5.6	53.7	52.3	51.3	51.3	46.4	46.4	46.1	46.5	39.6
400-600° F	16.4	12.5	11.4	10.7	10.4	10.0	11.3	16.8	19.2	18.2
600° F +	10.7	2.6	3.3	3.8	15.6	18.1	16.9	16.4	15.9	14.4

TABLE V

Dist. at C ₁₀ 400° F. Cut	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
API Grav	31.4	36.1	34.0	33.6	33.8	33.5	34.7	34.3	32.7	32.4
R.P. Dist. Yr										
150	103	103	104	104	108	102	108	94	104	96
150 (Vol.)	136	128	130	132	136	134	132	118	131	126
200 (Vol.)	240	230	238	236	240	242	239	239	237	232
200 (Vol.)	294	292	290	288	292	292	292	296	298	290
Red Vapour	6.3	7.7	5.6	5.3	6.3	6.6	6.8	8.6	5.8	7.6
Residue	93.0	93.0	92.8	92.4	92.1	92.0	92.3	91.6	92.3	91.3
RON-3 max/	97.5	97.9	97.4	97.8	98.1	97.5	97.6	97.3	97.6	97.6
gal. TEL										
MDN	61.1	61.3	61.2	61.3	61.0	61.3	62.0	60.6	60.9	61.8
(Lower)										
MDN-3 max/	64.0	65.2	65.1	65.0	65.3	65.6	65.6	64.3	65.1	65.3
gal. TEL										

What is claimed

1. In a catalytic cracking process unit wherein a gas oil feed is cracked in a cracking zone at an elevated temperature in the presence of a cracking catalyst, the cracking catalyst is regenerated in a regeneration zone by burning coke off the catalyst, and catalyst is circulated between the cracking zone and the regeneration zone, the improvement for obtaining a naptha product of improved octane number comprising introducing sufficient of a nickel and vanadium metals-containing heavy feedstock with said gas oil feed introduced into the cracking zone to deposit nickel and vanadium metals on said catalyst and raise the nickel and vanadium metals content of said catalyst to a level ranging from about 1000 to about 4000 parts per million of said metals expressed as equivalent nickel, based on the weight of the catalyst, and maintaining said nickel and vanadium metals level on this catalyst by withdrawing high nickel and vanadium metals-containing catalyst and adding low nickel and vanadium metals-containing catalyst to the regeneration zone.

2. The process of claim 1 wherein the metals-containing heavy feedstock added to said gas oil feed is one having a final boiling point above 1050° F.

3. The process of claim 1 wherein the metals-containing heavy feedstock is added to said gas oil feed prior to the introduction of the feed into the cracking zone.

4. The process of claim 1 wherein the metals-containing heavy feedstock added with said gas oil feed is one characterized as containing from about 2 to about 1000 ppm of equivalent nickel based on the weight of said heavy feedstock.

5. The process of claim 1 wherein the metals-containing heavy feedstock is continuously added with said gas oil feed in amounts ranging above 0 percent to about 25 percent, based on the volume of the gas oil, fresh catalyst is added to the unit at a rate of about 0.05 pounds to about 0.50 pounds per barrel of gas oil feed processed,

and catalyst withdrawn at a rate sufficient to maintain the unit in balance.

6. The process of claim 1 wherein the gas oil feed both within a range of from about 600° F. to about 1050° F.

7. The process of claim 9 wherein the gas oil feed both within a range of from about 600° F. to about 1050° F. and the metals containing heavy feedstock is added to said gas oil feed prior to the introduction of the feed into the cracking zone.

8. The process of claim 1 wherein the catalyst comprises a crystalline alumino-silicate zeolite.

9. In a catalytic cracking process unit wherein a gas oil feed is cracked in a cracking zone at elevated temperature in the presence of cracking catalyst, the cracking catalyst is regenerated in a regeneration zone by burning coke off the catalyst and catalyst is circulated between the cracking zone and the regeneration zone, the improvement for obtaining a naptha product of improved octane number comprising introducing sufficient of a nickel and vanadium metals containing heavy feedstock with said gas oil feed introduced into the cracking zone to deposit nickel and vanadium metals on said catalyst and raise the nickel and vanadium metals content of said catalyst to a level ranging from about 1,000 to 30,000 parts per million of said metals expressed as equivalent nickel based on the weight of the catalyst and maintaining said nickel and vanadium metals level on the catalyst by withdrawing high nickel and vanadium metals-containing catalyst and adding low nickel and vanadium metals-containing catalyst to the regeneration zone.

10. The process of claim 9 wherein the level of metals maintained on the catalyst ranges from about 2500 to about 4000 ppm expressed as equivalent nickel.

11. The process of claim 9, wherein the metals-containing heavy feedstock added to said gas oil feed is one having a final boiling point above 1050° F.

12. The process of claim 9, wherein the metals-containing heavy feedstock is added to said gas oil feed prior to the introduction of the feed into the cracking zone.

13. The process of claim 9, wherein metals-containing heavy feedstock added with said gas oil feed is one characterized as containing from about 2 to about 1000 ppm of equivalent nickel, based on the weight of said heavy feedstock.

14. The process of claim 9, wherein metals-containing heavy feedstock is continuously added with said gas oil feed in amounts ranging from above 0 percent to about 25 percent based on the volume of gas oil, fresh catalyst is added to the unit at a rate of about 0.05 pounds to about 0.50 pounds per barrel of gas oil feed processed, and catalyst withdrawn at a rate sufficient to maintain the unit in balance.

15. The process of claim 9, wherein the gas oil feed both within a range from about 600° to about 1050° F.

16. The process of claim 14, wherein the gas oil feed both within a range of from about 600° F. to 1050° F. and the metals-containing heavy feedstock is added to

said gas oil feed prior to introduction of the feed into the cracking zone.

17. The process of claim 9, wherein the catalyst comprises a crystalline alumino-silicate zeolite.

18. In a catalytic cracking processing unit wherein a gas oil feed is cracked in a cracking zone at elevated temperature in the presence of cracking catalyst, the cracking catalyst is regenerated in a regeneration zone by burning coke off the catalyst and catalyst is circulated between the cracking zone and the regeneration zone, the improvement for obtaining a naptha product of improved octane number comprising introducing sufficient of a nickel and vanadium metals containing heavy feedstock with said gas oil feed introduced into the cracking zone to deposit nickel and vanadium metals on said catalyst and raise the nickel and vanadium metals content of said catalyst to a level ranging from substantially larger than 600 to 70,000 parts per million of said metals expressed as equivalent nickel based on the weight of the catalyst and maintaining said nickel and vanadium metals level on the catalyst by withdrawing high nickel and vanadium metals-containing catalyst and adding low nickel and vanadium metals-containing catalyst to the regeneration zone.

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES
SOLICITUD VIA PCT**

2020
Bogotá, D C , 14 de agosto de 2007

Abogado
EMILIO FERRERO
Apoderado

Solicitante W R Grace & Co-Conn - Exxonmobil Research & Engineering Company

ASUNTO	Radicación	04-1078
	Tramite	002
	Evento	001
	Actuacion	430
	Oficio	1020?
	Folios	017

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

1 Documentos estudiados

- | | | |
|-----|-------------------------|---|
| 1 1 | <u>Descripcion</u> | Folios 48 a 94 |
| 1 2 | <u>Reivindicaciones</u> | Folios 95 a 102 |
| 1 3 | <u>Priondad</u> | Folios 35 a 47 (Estados Unidos No 09/901,939
Del 10 de julio de 2001 |

2 Objeto de la invencion

- El titulo de la solicitud es **“REDUCCION DEL AZUFRE EN LA GASOLINA EN EL CRAQUEO CATALITICO FLUIDO”** (Folio 2)
- Esta invención se relaciona con la reduccion del azufre en la gasolina y otros productos del petroleo producidos por un proceso de craqueo catalitico En particular esta invención se relaciona con un proceso de craqueo catalitico mejorado, el cual suministra corrientes de producto de craqueo catalitico 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 los productos de craqueo de un proceso de craqueo catalitico fluido (FCC) en el cual una alimentación de hidrocarburos pesados que comprende compuestos de órganoazufre es craqueada cataliticamente en productos más livianos por medio de ponerla en contacto con un proceso de craqueo de recirculacion de catalizador ciclico con un inventano de catalizador de equilibrio de craqueo catalitico fluidizable circulante, el proceso comprende

- (i) Suministrar una corriente de alimentación de hidrocarburos pesados sustancialmente líquidos que comprende por lo menos un compuesto de organoazufre como impureza
- (ii) Introducir la corriente de alimentación de hidrocarburos en una unidad de reactor FCC que opera bajo condiciones de craqueo catalítico y que tiene un inventario circulante de una composición catalizadora de equilibrio,
- (iii) Remover una porción del inventario de catalizador de equilibrio de la unidad de reactor FCC mientras se reemplaza todo el inventario de catalizador de equilibrio removido de la unidad con catalizador fresco para crear un ambiente estable dentro de la unidad,
- (iv) Poner en contacto la corriente de alimentación de hidrocarburos con por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar la concentración de vanadio en o sobre el inventario de catalizador de equilibrio en cerca de 100 a cerca de 20000 ppm, en relación con la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador, y
- (v) Poner en contacto el inventario de catalizador de equilibrio en la unidad de reactor FCC con la corriente de alimentación de hidrocarburo que contiene vanadio bajo un ambiente estable para producir un efluente de zona de craqueo que comprende productos craqueados, incluyendo gasolina, que tienen un contenido de azufre reducido

En la reivindicación independiente 12 se plantea un proceso mejorado para craqueo catalítico de un material de partida de hidrocarburos que contiene por lo menos compuestos de azufre orgánicos comprende en contacto en un reactor de craqueo catalítico fluido (FCC) un inventario de catalizador de equilibrio de craqueo catalítico fluido, remover una porción del inventario de catalizador mientras se reemplaza la misma cantidad de composición catalizadora fresca para suministrar un ambiente estable dentro del reactor FCC, la mejora comprende

- (i) Poner en contacto la alimentación de hidrocarburo con por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar la concentración de vanadio en o sobre el inventario de catalizador de craqueo de fluido de equilibrio en cerca de 100 a cerca de 20000 ppm, con relación a la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador,
 - (ii) Poner en contacto el catalizador de equilibrio con la alimentación de hidrocarburo que contiene vanadio en una unidad de reactor FCC bajo ambiente estable para producir un efluente de zona de craqueo que comprende productos craqueados, incluyendo gasolina, que tienen 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, continua 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 invencion definido se catalogo como **C10G 11/05** y **C10G 11/18**, segun la Clasificación Internacional de Patentes (IPC)

3 Determinación del Estado de la Técnica

Considerando que la fecha de presentación de la primera solicitud de patente de la cual se reivindica prioridad es **10 de julio de 2001**, se buscaron documentos del estado de la técnica relacionados y se encontro el siguiente documento

N°	Documento	Título	Fecha de Publicación
D1	US4728416	"CRACKING BLENDS OF GAS AND OIL AND RESIDUAL OIL"	1 de marzo de 1988

- Comentaros sobre el estado de la técnica

En el documento **US4728416** (D1) se divulga un proceso de craqueo catalitico 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 calefaccion 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 alimentacion 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 indice de octano además que puede ser un contaminante potencial del aire dado que al quemarse genera dióxido y tnoxido de azufre (Columna 8, lineas 9 – 20)

El proceso divulgado en D1 se lleva a cabo en una unidad de proceso de craqueo catalitico donde una alimentacion 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 compuesto de vanadio junto con la alimentacion del reactor para depositar dicho vanadio sobre el catalizador para aumentar el contenido de vanadio en dicho catalizador hasta un nivel entre 1500 y 6000 ppm y mantener dicho nivel retirando catalizador con vanadio hacia la zona de regeneracion (Columna 39, reivindicacion 1)

4 Análisis de patentabilidad (articulo 14 D486)

4 1 Novedad (articulo 16 D486)

- En las reivindicaciones de la solicitud en estudio se planea un proceso para reducir el contenido de azufre en productos del craqueo catalitico FCC mediante suministrar una corriente de alimentacion de hidrocarburos impuros en azufre, introducir la corriente en el reactor FCC bajo condiciones de craqueo catalitico teniendo un inventano circulante de una composicion catalizadora en equilibrio, remover una porcion del catalizador mientras se reemplaza para estabilizar el ambiente del reactor, poner en contacto la corriente de alimentacion de hidrocarburos con compuestos de vanadio para incrementar la concentración de este sobre el catalizador cerca de 100 a 20000 ppm y poner en contacto el inventano de catalizador con la corriente de alimentacion de hidrocarburo para producir un efluente de zona de craqueo que comprende los productos craqueados incluyendo gasolina con contenido de azufre reducido

La invención propuesta con 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 regenerarlo 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)

En la reivindicación dependiente 2 de la solicitud se especifica que el proceso comprende adicionalmente producir de manera simultánea un catalizador de gasto que contiene coque e hidrocarburos separables Sin embargo en D1 también se hace mención de ello (Columna 5, líneas 5 – 35)

En la reivindicación dependiente 3 se especifica que en el proceso además se descarga y separa la mezcla en fase vapor y la fase nca en sólidos, y se retira la fase de vapor para producir gasolina No obstante, en la figura 2 se diagrama este asunto

En las reivindicaciones 4 y 5 se alude a la naturaleza química del compuesto de vanadio Sin embargo en D1 se hace mención de sulfuros, sulfatos y óxidos de metal (Vanadio por ejemplo) depositados sobre las partículas de catalizador por previa exposición a una alimentación carbometálica y condiciones de regeneración (Columna 11, líneas 1 – 10)

En las reivindicaciones 6 y 7 se hace mención de los intervalos de concentración de vanadio sobre el catalizador Sin embargo, en la reivindicación 1 de D1 se divulga un intervalo que cae dentro del propuesto

En la reivindicación 8 se especifica que el catalizador comprende zeolita con tamaño de poro grande pero en D1 se explica que el catalizador comprende matrices con poros que tienen diámetros grandes y ranuras grandes para facilitar la difusión de moléculas de alto peso a través de la matriz (Columna 17 líneas 7 – 11)

En la reivindicación 9 se especifica que la zeolita con tamaño grande comprende una faujasita Sin embargo, en D1 se explica que las zeolitas aluminosilicatos cristalinos tienen una estructura de cristal tipo faujasita particularmente preferidas en la invención (Columna 15, líneas 41 – 45)

En las reivindicaciones 10 y 11 menciona que la alimentación también contiene vanadio y níquel como impurezas, cosa que en D1 también se divulga cuando se analiza las composiciones de las corrientes de alimentación (Ver tabla 1 entre columnas 37 y 38)

En la reivindicación 13 se menciona que el proceso también implica separar la fase de catalizador nca en sólidos para remover los hidrocarburos, transportar el catalizador separado al regenerador de catalizador, regenerar el catalizador al ponerlo en contacto con un gas que contiene oxígeno para producir un catalizador regenerado y reciclar el catalizador regenerado Sin embargo dichas operaciones también se realizan en el proceso de D1 según se aprecia en la figura 2

Así las cosas, el proceso definido en las reivindicaciones 1 a 13 no parece ser novedoso como se requiere según el art 16 de la Decisión 486

127

460

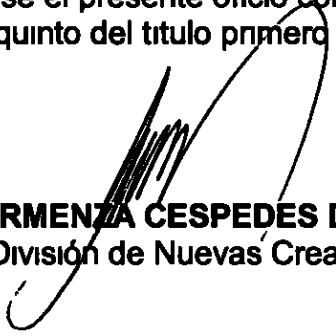
5 Conclusión

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

Nº	Documento Nº	Reivindicaciones Afectadas	Requisito que Afecta
D1	US4728416	1 – 13	Novedad

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 **sesenta 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 No. 10 de 2001


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 24 AGO 2007

CONCEPTO TECNICO No. 1296	EXAMINADOR TECNICO Codigo No. 202042
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