

LOW PRESSURE NAPHTHA HYDROCRACKING PROCESS

This invention is directed to naphtha, kerosene or diesel hydrocracking processes
5 employing large pore zeolite catalysts such as Zeolite Beta or Ultra Stable Y (USY), which are loaded with noble metals such as Pt or Pd or with transition metals such as Ni in combination with Mo or W. Preferably, low hydrogen partial pressures and a feedstock relatively rich in hydrogen are employed, in order to prevent catalyst aging.

Many refineries have been required to reduce the T_{90} (temperature at which 90% of the
10 gasoline pool boils as measured by an atmospheric distillation such as ASTM D-86) of the gasoline pool in order to meet more stringent governmental regulations being enacted in some areas. This requires removal of heavy feeds, such as FCC gasoline, from the gasoline pool. Such heavy feeds then enter the kerosene market, potentially forcing the price of kerosene to drop. It is therefore desirable to find new uses for FCC gasoline and kerosene, boiling in the range from 149° to 204°C.
15 The process of the instant invention will enable refineries to convert these feeds to gasolines which meet the criteria of governmental entities such as the EPA and CARB.

Catalysts comprising large pore zeolites loaded with metals combinations such as Ni-Mo or Ni-W have been previously employed in hydrocracking applications. U.S. Patent No. 5,401,704 (Absil et al., hereafter Absil) discloses a hydrocracking process employing a catalyst comprising
20 small crystal zeolite Y. Preferred feeds possess at least 70 wt.% hydrocarbons having a boiling point of at least 204°C. Lighter feeds are desired in the instant invention. Zeolite Y may be loaded with a metal or combinations of metals for hydrogenation purposes, such as Pt, Pd, Ni-W or Co-Mo. Absil does not, however, teach the concept of extinction recycle hydrocracking at hydrogen partial pressures below 2758 kPa, as does the instant invention.

25 U.S. Patent No. 5,500,109 (Keville et al., hereafter Keville #1) discloses a hydrocracking catalyst which comprises a large pore zeolite (such as USY) loaded with metals combinations such as NiW. This catalyst is extruded with an alumina binder. The disclosure suggests, however, that feeds intended for use with this catalyst are gas oils and residua, rather than the lighter feeds of the instant invention. There is also no mention of extinction recycle hydrocracking.

30 U.S. Patent No. 5,378,671 (Keville et al., hereafter Keville #2) is also directed to hydrocracking of gas oils and residua with catalysts comprising large pore zeolites.

U.S. Patent No. 4,968,402 discloses a process for producing high octane gasoline from heavy feedstocks containing over 50 wt.% aromatics such as polynuclear aromatics. A catalyst comprising MCM-22 is employed, preferably loaded with NiW.

35 U.S. Patent No. 4,851,109 discloses a two-stage process for hydrocracking feeds such as coker gas oils, vacuum gas oils, as well as light and heavy cycle oils. In the first stage, the feed is hydrocracked with a catalyst comprising a large pore zeolite, such as zeolite Y or USY. The catalyst may be loaded with a hydrogenation component such as a NiW combination. In the second stage, hydroprocessing occurs over a catalyst comprising zeolite beta.

U.S. Patent No. 3,923,641 to Morrison and U.S. Patent No. 4,812,223 to Hickey, Jr. et al. teach the conversion of C_5^+ and C_6^+ naphthas over noble metal-containing zeolite Beta catalyst, preferably a steamed zeolite Beta catalyst. There is no mention of extinction recycle hydrocracking.

5 Figure 1 is a process flow diagram of the preferred embodiment of the instant invention.

Figure 2 illustrates the results of a catalyst aging study, employing hydrocracked kerosene feed.

Figure 3 illustrates the results of a catalyst aging study, employing raw unhydrotreated FCC heavy naphtha.

10 A large pore zeolite cracking catalyst, loaded with noble metals such as Pt or Pd or with a transition metal such as Ni, in combination with a non-noble metal such as molybdenum or tungsten, is employed in a process to convert heavy naphtha, kerosene or diesel fractions (149° to 482°C endpoint) to lower boiling naphtha fractions, having a 149°C endpoint. The process is conceived to operate at hydrogen partial pressures in the range of 1480 to 69049 kPa, preferably
15 between 2170 to 37333 kPa), with up to full conversion of the heavy fraction by means of extinction recycle.

Large pore zeolite catalysts comprising noble metal or non-noble metals combinations have been considered to be unstable for extinction recycle hydrocracking at low hydrogen partial pressures. The instant invention demonstrates, however, that such catalysts may be used.

20 The low pressure hydrocracking process of the instant invention is illustrated in Figure 1. Fresh feed enters through line 1. The fresh liquid feed is specified to contain hydrogen and (i.e., sulfur, nitrogen and oxygen) to be consistent with the choice of catalyst metal function and the desired product properties. The boiling range for the feed is 121° to 482°C. The endpoint specification for the feed is 204° to 454°C. Liquid feed is mixed with hydrogen gas entering from
25 line 2, and the mixture enters reactor 100 via line 3. The mixture is distributed over at least two beds of packed catalyst particles in reactor 100. Additional gas and liquid may be injected between catalyst beds (as a quench) to control reactor temperature. Total pressure in reactor 1 can range from 2170 to 10443 kPa, and hydrogen partial pressure will range from 1480 to 69049 kPa. Reactor temperatures are adjusted to give the desired level of boiling point conversion, but will
30 typically range from 232° to 454°C.

The effluent from reactor 100 enters the gas-liquid separator 200 via line 4. Liquid product is drawn from the bottom of the separator and sent via line 7 to splitter column 300. Hydrocarbons boiling below 149°C go overhead in splitter column 300, and higher boiling components are taken from the bottom and recycled. The recycle liquid is sent through line 8 and mixed with fresh feed. If
35 desired, a portion of the recycle liquid may be withdrawn as a product stream, producing a product of higher quality than the feed. In the event that the catalyst generates significant quantities of C4-compounds, a stabilizer column can be inserted in the process flow prior to splitter 300. The embodiment depicted in Figure 1 shows the overhead from splitter column 300 passing through line

9 to stabilizer 400. Product naphtha with a 149°C endpoint is drawn from the bottom of the stabilizer (line 10), and C4- is taken overhead (line 11).

Gas in the reactor effluent is taken from the top of separator 200 via line 5 and recycled back to reactor 100. Recycle gas is mixed with fresh hydrogen make-up gas from line 2 to control hydrogen purity. This is particularly important if significant quantities of methane and ethane are generated in the process. The recycle gas rate will range from 712 to 2136 n.l.l.⁻¹ of feed. Hydrogen purity in the recycle gas should be maintained above 75 mol.%.

Feed

The feed to this process comprises a heavy naphtha, kerosene, or diesel characterized by a boiling range of C₁₁ to C₁₅ (approximately 93° to 482°C, more preferably 149° to 427°C). Sources of this feed include straight run naphtha, hydrocracked naphtha, pretreated reformer feed, fluid catalytically cracked (FCC) naphtha, heavy naphtha or light cycle oil feed, coker naphtha, coker kerosene, or coker gas oil. The choice of the preferred catalyst metal function is dependent on the quality of the feedstock processed and the desired product quality. Noble metal catalyst formulations are preferred for clean feeds, while base metal catalyst formulations are preferred for feedstocks containing high levels of heteroatoms or for operations where higher hydrocracked product octanes are desired.

For the noble metal loaded catalysts the aromatics content of the feed should be no greater than 30 wt.%, and the naphthenic content between 40 and 70 wt.%. The range of API gravity for the feed is between 25 and 50. Since a total hydrogen content above 13.0 wt.% and a total heteroatom level below 500 ppmw is required, it may be necessary to hydrotreat the feed prior to hydrocracking according to the instant invention. Total hydrogen is defined as the sum of hydrogen in the gas and liquid feeds minus the amount of hydrogen predicted to be consumed by sulfur and nitrogen as hydrogen sulfide and ammonia, respectively, expressed as weight percent of the feed.

For the base-metal loaded catalysts the aromatics content of the feed should be no greater than 40 wt.%, and the naphthenic content between 30 and 60 wt.%. The range of API gravity for the feed is between 25 and 50. Since base metal catalysts can tolerate elevated levels of heteroatoms, pretreatment of the feed is not required. In this case the total heteroatom content should be less than 2 wt.%.

Feedstocks suitable for low pressure hydroconversion are heavy naphtha, kerosene or diesel from a single stage or two-stage hydrocracking process or cracked naphthas which have been subjected to hydrotreating at conditions that will meet the feedstock quality, such as pretreated FCC naphtha, kerosene or light cycle oil, coker naphtha or gas oil.

If it is necessary to hydrotreat the feed, conventional hydrotreating catalysts and conditions may be employed. The hydrotreating catalyst typically comprises a base metal hydrogenation function on a relatively inert, i.e. non-acidic porous support material such as alumina, silica or silica alumina. Suitable metal functions include the metals of Groups VI and VIII of the Periodic Table, preferably cobalt, nickel, molybdenum, vanadium and tungsten. Combinations of these metals such as cobalt-molybdenum and nickel-molybdenum will usually be preferred. Operating conditions

of liquid hourly space velocity (LHSV), hydrogen circulation rate and hydrogen pressure will be dictated by the requirements of the hydrocracking step, as described below. Temperature conditions may be varied according to feed characteristics and catalyst activity in a conventional manner.

Reference is made to U.S. Patent No. 4,738,766 for a more detailed description of suitable hydrotreating catalysts and conditions which may also be suitably employed in the present process.

Catalyst

The preferred hydrocracking catalysts for use in the present process are the zeolite catalysts, comprising a large pore size zeolite, usually composited with a binder.

The large pore size zeolites such as zeolites X, Y, and Beta are preferred in order to effect the desired conversion of naphthenes and aromatics in the feeds to produce the aromatic, high octane gasoline product.

Suitable hydrocracking catalysts include those solids having relatively large pores which exhibit both acid and hydrogenation functions. The acid function is therefore suitably provided by a large pore size aluminosilicate zeolite characterized by a Constraint Index of less than 2, examples of which include mordenite, TEA mordenite, zeolite X, zeolite Y, ZSM-4, ZSM-12, ZSM-20, ZSM-38, ZSM-50, REX, REY, USY and Beta. The zeolites may be used in certain of their various forms, for example, certain of their cationic forms, preferably cationic forms of enhanced hydrothermal stability. For example, rare earth exchanged large pore zeolites such as REX and REY are generally preferred, as are the ultra-stable zeolite Y (USY) and high silica zeolites such as dealuminized Y or dealuminized mordenite or beta.

An especially preferred hydrocracking catalyst is based on the ultra-stable zeolite Y (USY) with base metal hydrogenation components selected from Groups VIA and VIIIA of the Periodic Table (IUPAC Table). Combinations of Groups VIA and VIIIA metals are especially favorable for hydrocracking, for example nickel-tungsten, nickel-molybdenum, et al. Other useful hydrocracking catalysts comprise USY or beta composited with noble metals.

A more extensive and detailed description of suitable catalysts for the present process may be found in U.S. Patent Nos. 4,676,887; 4,738,766 and 4,789,457 to which reference is made for a disclosure of useful hydrocracking catalysts.

A convenient measure of the extent to which a zeolite provides control to molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. The method by which Constraint Index is determined is described in U.S. Patent No. 4,016,218. U.S. Patent No. 4,696,732 discloses Constraint Index values for typical zeolite materials.

The above-described Constraint Index provides a definition of those zeolites which are useful in the instant invention. The very nature of this parameter and the recited technique by which it is determined, however, admit the possibility that a given zeolite can be tested under somewhat different conditions and thereby exhibit different Constraint Indices. Constraint Index seems to vary somewhat with the severity of operations (conversion) and the presence or absence of binders. Likewise, other variables, such as crystal size of the zeolite, and the presence of occluded

contaminants, etc., may affect the Constraint Index. Therefore, it will be appreciated that it may be possible to select test conditions, e.g., temperature, so as to establish more than one value for the Constraint Index of a particular zeolite. This explains the range of Constraint Indices for some zeolites such as ZSM-5, ZSM-11 and Beta.

5 The hydrogenation function is provided by a metal or combination of metals. Noble metals of Group VIIIA of the Periodic Table, especially platinum or palladium may be used, as may base metals of Groups IVA, VIA, and VIIA, especially chromium, molybdenum, tungsten, cobalt and nickel. Combinations of metals such as nickel-molybdenum, cobalt-molybdenum, cobalt-nickel, nickel-tungsten, cobalt-nickel-molybdenum, and nickel-tungsten-titanium can be effective. The
10 non-noble metals are often used in the form of their sulfides.

 In practicing conversion processes using the catalyst of the present invention, it may be useful to incorporate the above-described crystalline zeolites with a matrix comprising another material resistant to the temperature and other conditions employed in such processes. Such matrix materials include synthetic or naturally occurring substances, as well as inorganic materials
15 such as clay, silica and/or metal oxides, most notably alumina oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main
20 mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state or initially subjected to calcination, acid treatment or chemical modification.

 In addition to the foregoing materials, the zeolites employed herein may be composited with a porous matrix material, such as alumina, silica, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria silica-beryllia, and silica-titania, as well as ternary compositions such as silica-alumina-
25 thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix, on an anhydrous basis, may vary widely with the zeolite content ranging from between 1 to 99% and, more usually, in the range of 40 to 90% by weight of the dry composite.

 Additional catalyst modifying procedures which may also optionally be employed to modify
30 the activity or selectivity include precoking and presteaming or combination thereof. Presteaming, preferably conducted at 204° to 427°C for 0.25 to 24 hours and with 10 to 100% steam, generally alters zeolite catalyst activity and selectivity.

 The noble metals useful in the hydrocracking catalyst include platinum, palladium, and other Group VIIIA metals such as iridium and rhodium with platinum or palladium preferred as
35 noted above. The noble metal may be incorporated into the catalyst by any suitable method such as impregnation or exchange the zeolite. The noble metal may be incorporated in the form as cationic, anionic or neutral complex such as $\text{Pt}(\text{NH}_3)_4^{2+}$, and cationic complexes of this type will be found convenient for exchanging metals into the zeolite. The amount of noble metal is suitably from 0.01 to 10% by weight, normally from 0.1 to 2.0% by weight. In a preferred method of

synthesizing Pt-containing zeolite Beta or USY the platinum compound is tetraamineplatinum hydroxide. The noble metal is preferably introduced into the catalyst composition with a pH near-neutral solution.

A high level of noble metal dispersion is preferred. For example, platinum dispersion is measured by the hydrogen chemisorption technique and is expressed in terms of H/Pt ratio. The higher the H/Pt ratio, the higher the platinum dispersion. Preferably the resulting catalyst should have a H/Pt ratio greater than 0.7.

Conditions

The hydrocracking conditions employed in the present process are generally those of low hydrogen pressure and moderate hydrocracking severity. Hydrogen pressure reactor inlet) is maintained from 2170 to 69049 kPa. Hydrogen circulation rates of between 356 to 1780 n.l.l.⁻¹, more usually between 534 to 1246 n.l.l.⁻¹ are suitable, with additional hydrogen supplied as quench to the hydrocracking zone, usually in comparable amounts. Space velocity is between 1 and 2 LHSV.

Temperatures are maintained usually in the range of 232° to 454°C, and more usually will be in the range of 246° to 427°C. A more preferred operating range is 260° to 413°C. Thus, the selected temperature will depend upon the catalyst formulation employed, the character of the feed, hydrogen pressure employed and the desired conversion level.

Conversion is maintained at relatively moderate levels and, as noted above, will usually not exceed 60 wt.% to gasoline boiling range material per pass. Since extinction recycle is employed, however, the feed will ultimately be totally converted to materials boiling below 149°C. Alternatively, a portion of the liquid recycle may be withdrawn to produce a product of higher quality than the feedstock.

Examples

Laboratory Data

The proposed process was demonstrated using a laboratory pilot unit equipped with an on-line still, and gas recycle system.

The support of Catalyst A comprises 65 wt.% USY and 35 wt.% alumina binder. Catalyst A is loaded with Ni-W, as described in U.S. Patent No. 5,219,814. The alpha value is 25.45.

The support of Catalyst B comprises 65 wt.% zeolite beta and 35 wt.% alumina binder. It is loaded with 0.6 wt. Pt, based on the total wt. of the catalyst. The zeolite beta is unsteamed.

The support of Catalyst C comprises 65 wt.% USY and 35 wt.% alumina binder. It possesses an alpha value of 25.3, and is loaded with Pt. The zeolite beta is unsteamed.

Catalyst A was first sulfided with a 2% hydrogen sulfide in hydrogen gas mixture according to standard sulfiding procedures. Catalysts B and C were first sulfided with a 400 ppmv hydrogen sulfide in hydrogen gas mixture according to standard sulfiding procedures. Hydrogen gas was then circulated at a target rate equivalent to 712 to 1246 n.l.l.⁻¹ when running at 0.9 to 1.4 total LHSV, and pressure was set at 2785 kPa total. The reactor was heated to 149°C before introducing a hydrocracked kerosene feed. A raw unhydrotreated FCC heavy naphtha was also tested.

Feedstock properties are shown in Table 1. The unit was lined out at 60 vol.% conversion to 149°C product per pass, with recycle of the on-line still bottoms to extinction. Product properties are shown in Table 2.

The process concept was evaluated by evaluating the performance of Catalyst A, Catalyst B and Catalyst C processing the HDC kerosene. In addition, Catalyst A was evaluated processing raw FCC heavy naphtha.

To distinguish the proposed concept from generally accepted views that hydrocracking catalysts such as Pt, Pd or base metal hydrocracking catalysts such as NiW/USY catalysts rapidly age at low reactor pressures, it was important to test catalyst stability. Consequently, the Ni-W pilot unit study was continued for approximately 40 days to measure aging. Figure 2 shows a plot of catalyst activity as a function of time on-stream. Catalyst A appeared to age rapidly as would be expected during the initial 15 days on-stream but, quite unexpectedly, stabilized to an acceptable aging rate of 0.35°C/day after 30 days on-stream. It is reasonably expected that even lower aging rates can be attained by further optimizing the hydrogen circulation rate. It is further expected that adding a hydrotreating catalyst upstream of the Ni-W USY catalyst could further reduce apparent catalyst aging rate.

Catalysts B and C aging performance was also evaluated and both catalysts aged at less than 0.005°C per day.

Flexibility of the current process configuration is demonstrated by the data obtained switching after 40 days on-stream from the hydrocracked kerosene feed to a raw heavy FCC naphtha (Table 1). The FCC naphtha contained only 11.4 wt.% hydrogen compared to 13.4 wt.% hydrogen in the hydrocracked kerosene. As shown in Figure 3, surprisingly, stable extinction recycle hydrocracking performance is attained, albeit at higher required reactor inlet temperature.

Table 1. Feed Properties			
	Feedstock		Feedstock
	Hydrocracked Kerosene		FCC Gasoline
	API	43.4	32.3
	S, ppmw	<20	6000
	N, ppmw	<0.5	270
	H, wt. %	13.6	11.0
	<u>Boiling Range by</u>		
	<u>D2887. °C</u>		
	IBP	114	118
	10 wt. %	139	145
	30%	158	169
	50%	168	184
	70%	180	202
	90%	193	222
	EP	214	248
	<u>PNA Analysis, wt. %</u>		
	Paraffins	13.6	--
	Naphthenes	69.1	--
	Aromatics	17.3	75

Table 2. Product Properties

5	Catalyst	A	A	B	C
	Feedstock	HDC Kero	FCC Heavy Naphtha	HDC Kero	HDC Kero
10	<u>Pilot Unit Conditions</u>				
	Total LHSV 1.4	1.4	0.91	1.4	
15	Total Pressure, kPa	2756	2770	2756	2756
	Hydrogen Pressure at Rx Inlet, kPa	2411	2425	2411	2411
	Rx Temperature, °C 288	338	394	271	
20	Gas Circulation, n.l.l. ⁻¹ 712	1157	1317	712	
	Conv. to 149°C W/recycle to Extinction	60	60	60	60
25	<u>Product Yields, wt. %</u>				
	C1 + C2	1.45	5.83	0.04	0.17
	C3	4.94	9.31	2.54	2.83
	iC4	16.39	12.14	22.68	15.81
	nC4	4.17	6.78	1.91	
30	2.79				
	C5 - 149°C	23.5	21	23.6	26
	149°C+	0.00	0.00	0.00	
	1.3				
35	H2 Consumption, n.l.l. ⁻¹ 174	160	38.3	18.7	
	C4 selectivity, %	20	19	25	18
	C5 - 149°C Selectivity, %	75	70	75	79
	C5 + Aromatics, wt. %	15	45	-	-
40	<u>C5+ Gasoline Properties</u>				
	R+0	85.5	93.0	-	-
	M+0	79.9	84.4	-	-
45	R+M/2	82.7	88.7	82.5	
	71.5				

CLAIMS:

1. A low pressure hydrocracking process in which catalyst cycle length is extended, the process comprising the following steps:

(a) mixing a liquid feed which comprises at least 13.0 wt.% total hydrogen, and less than 2 wt.% heteroatoms, with hydrogen gas, wherein the feed boils in the range from 121° to 482°C, having an aromatic content of less than 75 wt.% and an API gravity between 25 and 50;

(b) hydrocracking said mixture in a fixed bed hydrocracker which possesses at least two beds of packed catalyst particles, wherein said catalyst comprises a large pore zeolite formulated with a hydrogenation function, a hydrogen partial pressure in the range from 1379 to 6895 kPa, producing a lighter fraction which boils below 149°C and a heavier fraction which boils between 149° and 482°C;

(c) passing all or a portion of the fraction which boils between 149° to 482°C through an extinction recycle process in order to convert the fraction to desirable products, the process comprising the following steps:

(1) passing the material to be recycled to a hydrocracker, where it is combined with hydrogen and undergoes cracking at a hydrogen partial pressure in the range from 2170 to 69049 kPa, producing a lighter fraction which boils below 149°C and a heavier fraction which boils between 149° and 482°C;

(2) recycling the heavier fraction of the effluent of step (1) to step (1) until it has been totally converted to a fraction boiling below 149°C.

2. The process of claim 1 step(c)(1), wherein the rate of conversion to a lighter fraction boiling below 149°C is 60 wt.%.

3. The process of claim 1(a), wherein a gas or liquid may be injected into the hydrocracker as a quench in order to control reactor bed temperature.

4. The process of claim 1, wherein the large pore zeolite of the hydrocracking catalyst is selected from the group consisting of zeolite X, zeolite Y and USY, zeolite beta, REX, REY, mordenite, ZSM-4, ZSM-20, ZSM-12, ZSM-38 and ZSM-50.

5. The process of claim 4, wherein the large pore zeolite further comprises a base metal combination.



6. The process of claim 4 wherein the feed of claim 1(a) is contacted by a hydrotreating catalyst which is loaded with base metals prior to contacting the hydrocracking catalyst of claim 1 step(b).
7. The process of claim 4 wherein the hydrocracking catalyst stabilizes to an aging rate of 0.36°C/day after 30 days on stream.
8. The process of claim 4, wherein the large pore zeolite of the hydrocracking catalyst has a Constraint Index less than 2.
9. The process of claim 4, wherein the large pore zeolite further comprises a noble metal or a combination of noble metals.
10. The process of claim 9, wherein the noble metal is Pt.

