

MIDDISTILLATE PRODUCTION

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This invention relates to a process for selectively producing middistillate hydrocarbons.

One of the most important characteristics that a modern petroleum refinery must have is flexibility. The ability to use different feedstocks, ranging from shale oils and heavy oils to light oils, to produce different product requirements in response to changing consumer demands is crucial to profitability. Feedstocks, for example, are now shifting to higher boiling, lower quality mixtures having more metal, nitrogen and sulfur contaminants than feeds previously used. Forecasts of consumer demand are predicting shifts from gasoline-range hydrocarbons to heavier, higher boiling products such as diesel fuels, fuel oils and turbine fuels.

Hydrocracking, used either in a one-step process or multistep processes coupled with hydrodesulfurization and hydrodenitrogenation steps, has been used extensively to upgrade poor-quality feeds and to produce gasoline-range materials. Over the years, much development work has gone into finding improved hydrocracking conditions and catalysts. Tests have used catalysts containing only amorphous materials and catalysts containing zeolites composited with amorphous materials.

Among the zeolites disclosed in the patent literature are Y (U.S. 3,130,007); decationized Y (U.S. 3,130,006); ultrastable Z-14US (U.S. 3,293,192 and U.S. 3,449,070); ultrastable Y (U.S. 3,536,605) and ultrahydrophobic Y (U.K. 2,014,970 published September 5, 1979). Disclosures have appeared which relate to modifying zeolites. U.S. 3,367,884 discloses reducing the activity of superactive zeolites by a calcining, leaching procedure. The catalyst is disclosed as being especially useful for cracking gas oils to gasoline. U.S. 3,506,400 and U.S. 3,591,488 disclose improving the stability of the crystalline lattice of zeolites by a steaming and acid extraction process. The product, a stabilized zeolite, may be used in hydrocracking and is disclosed as having improved selectively

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1 as shown by higher gasoline yield and lower coke make.

Other research has resulted in disclosures relating to producing midbarrel products. U.S. 3,853,72 discloses hydrocracking high boiling feeds to produce
5 midbarrel products using a catalyst containing a steamed zeolite. U.S. 4,120,825 also discloses improving the production of midbarrel products by hydrocracking with a catalyst containing a steamed zeolite.

We have discovered that middistillate products
10 can be selectively produced by hydrocracking with an expanded-pore zeolitic catalyst.

Thus in accordance with the present invention, there is provided a process for selectively producing a middistillate hydrocarbon product of which more than 40
15 percent by volume boils above 300°F (149°C) and below 700°F (371°C), which comprises:

(a) contacting under hydrocracking conditions a hydrocarbonaceous feed boiling above 600°F (316°C) with a catalyst comprising a hydrogenation component and an
20 expanded pore zeolite on a refractory inorganic oxide support, the zeolite being a faujasitic zeolite which has been steamed and then dealuminated; and

(b) recovering as effluent the desired middistillate product.

25 We have discovered that faujasitic zeolites which have been dealuminated after high-temperature steaming have surprising stability and activity for producing middistillates from higher-boiling feeds. By faujasitic zeolites are meant crystalline aluminosilicates, synthetic or natural, which have the crystalline structure
30 of the large-pore zeolite, faujasite. These zeolites include faujasite, zeolite X, zeolite Y, and zeolites derived from them. For example, there are numerous processes known to the art for treating zeolite Y to
35 produce "decationized Y", "ultrastable Y", "Z14-US", and others. The preferred faujasitic zeolite is zeolite Y, as well as derivative zeolites having the crystal lattice characteristics of zeolite Y. The most prefer-

16 1 red faujasitic zeolite is an ultrastable Y zeolite having a sodium content of less than 0.5 wt. % (as Na_2O).

5 As prepared, the large pore zeolites typically contain significant amounts of alkali metal. Because the alkali metals tend to poison the acid sites of the zeolite, standard ion-exchange procedures are used to remove them. The alkali metal content (calculated as oxide) is preferably reduced to below 5 weight percent
10 before any heat treatments, and to less than 200 ppm by weight in the final zeolite.

The faujasitic zeolite being treated is calcined at high temperatures in the presence of water which is preferably stagnant, i.e. non-flowing. During this high-temperature
15 steaming, it is desired that at least 2 weight percent of the atmosphere above the zeolite be water, preferably more than 10 weight percent, more preferably greater than 25 weight percent. The most convenient way to calcine the zeolite is to place the zeolite which has
20 undergone aqueous ion exchange into an autoclave and allow steaming to take place under autogenous pressure. The temperature of the steaming step is normally above 1000°F (538°C), preferably above 1200°F (649°C), and most preferably above 1400°F (760°C). The time of the
25 steam calcining can range from one-half hour to twenty-four hours or more.

It appears that the steam calcining causes aluminum to be removed from the crystal lattice and silicon to be volatilized to repair the holes left in the
30 lattice by the aluminum. Thus, the integrity of the lattice is largely maintained and total collapse is avoided. Nevertheless, there is some loss of crystallinity. The steaming also creates gross cracks and fissures in the crystalline particles. The aluminum
35 removed from the lattice appears to form amorphous alumina deposits in the lattice pores and channels. These amorphous deposits are removed by the dealumination procedure. Dealumination typically involves leaching the

1 steamed zeolite with organic chelating agents such as EDTA
or with organic or inorganic acids. Dilute inorganic
acids, particularly hydrochloric acid and sulfuric acid,
are most preferred. Where acids are used, the pH of the
5 leaching solution is preferably below about 2. It can be
appreciated that if the pH is too high, dealumination will
take inconveniently long, while if the acid concentration
is too high, the zeolite's crystal lattice can be
attacked. Typical acid solutions are from about 0.01 N to
10 about 10 N.

The final zeolitic product will have a smaller
crystal lattice and a higher silica:alumina mole ratio
than is normally obtained. Steamed, dealuminated zeolite
Y will typically have a cubic cell constant less than
15 about 24.40 Angstroms and a silica:alumina mole ratio
greater than about 10:1, and most preferably greater than
about 20:1. The final dealuminated product will also have
a higher surface area than the starting material. The
steaming/calcining treatment surprisingly also improves
20 the catalytic characteristics of ultrastable Y zeolites.
Even though the alumina content of the steamed/leached
faujasitic zeolites is very low compared to the starting
materials, they retain surprising activity and they gain
significant selectivity for the valuable middistillates.

25 The final catalyst composite includes both the
faujasitic zeolite and a refractory inorganic oxide matrix. Inor-
ganic oxides are standard supports for zeolites used in
hydroprocessing and can include alumina, silica, magnesia,
titania, and combinations thereof. The preferred support
30 is alumina. A wide variety of procedures can be used to
combine the zeolite with the refractory oxide. For
example, the zeolite can be milled with a hydrogel of the
oxide followed by partial drying if required and extruding
or pelletizing to form particles of the desired shape.
35 Alternatively, the refractory oxide can be precipitated in
the presence of the zeolite. This is accomplished by
increasing the pH of the solution of a refractory oxide
precursor such as sodium aluminate or sodium silicate. As

1 described above, the combination can then be partially,
dried as desired, tableted, pelleted, extruded, or formed
by other means and then calcined, e.g., at a temperature
above 600°F (316°C), usually above 800°F (427°C).

5 Processes which produce larger pore size supports are
preferred to those producing smaller pore size supports
when cogelling. Additionally, if the steamed zeolite is
added to an acidic solution of inorganic oxide precursor,
the leaching step can be carried out in situ in the
10 cogellation mixture without a separate leaching step.

The catalyst should advantageously contain less than 50,
preferably less than 30 weight percent of the
zeolite based on the dry weight of zeolite and refractory
inorganic oxide. However, the zeolite content should advanta-
15 geously exceed 0.5 and is usually above 2 weight percent.

The final catalyst composite includes at least
one hydrogenation component. The hydrogenation component
is typically a transition or Group IV-A metal, and is
usually a Group VI-B or VIII metal or combination of
20 metals or their oxides or sulfides.

The hydrogenation components preferably are
molybdenum, tungsten, nickel and cobalt metals, oxides and
sulfides. Preferred compositions contain more than
5 weight percent, preferably 5 to 40 weight
25 percent molybdenum or tungsten or both, and at least
0.5, and generally 1 to 15 weight percent of
nickel or cobalt or both, determined as the corresponding
oxides. The catalysts are often presulfided before use as
sulfide form of these metals tends to have higher
30 activity, selectivity and activity retention.

The hydrogenation components can be added by any
one of numerous procedures. They can be added either to
the zeolite or the support or a combination of both. In
the alternative, the Group VIII components can be added to
35 the zeolite by comulling, impregnation, or ion exchange
and the Group VI components, i.e., molybdenum and
tungsten, can be combined with the refractory oxide by
impregnation, comulling or co-precipitation.

1 The hydrogenation components can be incorporated
at any one of a number of stages in the catalyst prepara-
tion. For example, metal compounds such as the sulfides,
oxides or water-soluble salts such as ammonium hepta-
5 molybdate, ammonium tungstate, nickel nitrate and cobalt
sulfate can be added by comulling, impregnation or preci-
pitation to either the zeolite or the refractory oxide or
both before the zeolite is finally calcined and combined
with the support or after its final calcination but before
10 combination with the refractory oxide. These components
can be added to the finished catalyst particle by impreg-
nation with an aqueous or hydrocarbon solution of soluble
compounds or precursors.

 The hydrocarbonaceous feeds used in these processes
15 boil primarily above 600°F (316°C), generally above
700°F (371°C). Preferably, at least about 90 percent of
the feed will boil between about 700°F (371°C) and about
1200°F (649°C). Feedstocks having these characteristics include
gas oils, vacuum gas oils, coker gas oils, deasphalted
20 residua and catalytic cracking cycle stocks. The feed to
the hydrocracking zone generally contains at least about
5 ppm and usually between about 10 ppm and 0.1 weight
percent nitrogen as organonitrogen compounds. It can also
contain substantial amounts of mono- or polynuclear
25 aromatic compounds corresponding to at least about 5, and
generally about 5 to about 40 volume percent aromatics.

 Although the catalysts used in these methods
exhibit superior stability, activity and midbarrel selec-
tivity, reaction conditions must nevertheless be
30 correlated to provide the desired conversion rates while
minimizing conversion to less desired lower-boiling
products. The conditions required to meet these objec-
tives will depend on catalyst activity and selectivity and
feedstock characteristics such as boiling range, as well
35 as organonitrogen and aromatic content and structure.
They will also depend on the most judicious compromise of
overall activity, i.e., conversion per pass and selec-
tivity. For example, these systems can be operated at

01 relatively high conversion rates on the order of 70, 80 or
even 90 percent conversion per pass. However, higher
conversion rates generally result in lower selectivity.
Thus, a compromise must be drawn between conversion and
05 selectivity. The balancing of reaction conditions to
achieve the desired objectives is part of the ordinary
skill of the art.

Reaction temperatures generally exceed
500°F (260°C) and are usually above 600°F (316°C),
10 preferably between 600°F (316°C) and 900°F (482°C).
Hydrogen addition rates should generally be at least 400, and
are usually between 2,000 and 15,000 standard
cubic feet per barrel. Reaction pressures generally exceed 200 psig
(13.7 bar) and are usually within the range of 500
15 to 3000 psig (32.4 to 207 bar). Liquid hourly space
velocities are generally less than 15, preferably between
about 0.2 and about 10.

The overall conversion rate is primarily
controlled by reaction temperature and liquid hourly space
20 velocity. However, selectivity is generally inversely
proportional to reaction temperature. It is not as
severely affected by reduced space velocities at otherwise
constant conversion. Conversely, selectivity is usually
improved at higher pressures and hydrogen addition rates.
25 Thus, the most desirable conditions for the conversion of
a specific feed to a predetermined product can be best
obtained by converting the feed at several different
temperatures, pressure, space velocities and hydrogen
addition rates, correlating the effect of each of these
30 variables and selecting the best compromise of overall
conversion and selectivity.

The conditions should be chosen so that the
overall conversion rate will correspond to the production
of at least 40 percent, and preferably at least 50 percent
35 of products boiling above 300°F (149°C) and below 700°F
(371°C) per pass, i.e. in the middistillate range.

01 The process can maintain conversion levels in excess of
50 percent per pass at selectivities in excess of 60
percent to middistillate products boiling between 400°F
(204°C) and 700°F (371°C).

05 The process can be operated as a single-stage
hydroprocessing zone. It can also be the second stage of
a two-stage hydrocracking scheme in which the first stage
removes nitrogen and sulfur from the feedstock before
contact with the middistillate-producing catalyst. The
10 process can also be the first stage of a multistep
hydrocracking scheme. In operation as the first stage,
the middistillate-producing zone also denitrifies and
desulfurizes the feedstock; in addition, it allows the
second stage to operate more efficiently so that more
15 middistillates are produced overall than in other process
configurations. This method of operating with the
middistillate-producing step first, followed by at least
one further hydrocracking step is especially preferred
for increasing middistillate production.

20 In the accompanying drawings,

FIG. 1 illustrates the difference in fouling
rate and activity between a standard amorphous catalyst
used to produce middistillates and the catalyst used in the
invention.

25 FIG. 2 illustrates the effect of the amount of
acid used in the leaching solution on the silica:alumina
mole ratio of the zeolite.

FIG. 3 illustrates the effect of the amount of
acid used in the leaching solution on the crystallinity of
30 the product zeolite as compared to the reactant steamed
zeolite.

FIGS. 4, 5, and 6 illustrate the superiority of
the invention in producing middistillate. Catalysts con-
taining steamed/leached, steamed, and untreated ultra-
35 stable Y zeolites were contrasted. FIG. 4 illustrates the
higher middistillate diesel yields of the steamed/leached
catalyst; FIG. 5 illustrates the lower heavy naphtha
yields of the steamed/leached catalyst; and FIG. 6

illustrates the lower aromatics content of the middis-
tillate produced by the steamed/leached catalyst. The
yields are plotted against conversion to below 670°F
(354°C).

FIG. 7 contrasts the pore size distribution of a
steamed and steamed/leached Y zeolite.

The following Examples illustrate the invention.

Example 1

A catalyst containing steamed, leached Y zeolite
was compared to a nickel-tungsten, nonzeolitic catalyst
(silica/alumina/titania cogel base) used to prepare mid-
distillates to compare activity and fouling rates. The
zeolitic catalyst contained 15 weight percent zeolite
steamed at 1475°F (802°C) for 1 hour and washed with 1 N
hydrochloric acid. The zeolite was mulled with alumina
and had a final metals content of 3.9 weight percent
nickel and 20.5 weight percent tungsten. The feed was a
straight-run Arabian Heavy gas oil having the following
characteristics:

°API	21.8
Aniline Pt.	173°F (78°C)
S, Wt. %	2.62
N, ppm	846
Distillation (D-1160),	
°C:	
St/5	332 / 388
10/30	401 / 436
50	451
70/90	468 / 499
95/EP	514 / 540

Reaction conditions included an LHSV of 0.75; 1400 psig
(96.5 bar); and 5000 SCF H₂/bbl feed. The results are
shown in FIG. 1. The zeolitic catalyst is significantly
more active with a significantly lower fouling rate than
the nonzeolitic catalyst.

Example 2

A series of experiments was performed to examine the effect of acid washing on silica:alumina mole ratio and product zeolite crystallinity. The starting material was NH_4Y having a sodium content of less than 1 percent and a silica:alumina mole ratio of 5.1:1. The zeolite was steamed for 1 hour at 800°C and then acid washed. The washing solutions were prepared on the basis of volumes of concentrated hydrochloric acid per gram of the zeolite (0.8 ml concentrated HCl is the stoichiometric amount of acid required to raise the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio from 5:1 to 30:1), the measured acid was then diluted to about 1.1 M or 8.5 M and the zeolite was washed with the resulting solution. The silica:alumina mole ratio was determined by neutron activation analysis; percent crystallinity was measured as percent X-ray diffraction intensity relative to Na-Y. As can be seen from FIGS. 2 and 3, $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio and percent crystallinity appear to vary linearly and unexpectedly with the amount of acid used to prepare the washing solution rather than with the strength of the washing solution. It is preferred to retain at least 50 percent crystallinity measured as percent X-ray diffraction intensity relative to Na-Y in the product as compared to the starting material.

Example 3

A series of experiments was performed to compare the products obtained with different zeolitic hydrocracking catalysts. Catalysts A and B were steamed for 1 hour at 800°C and Catalyst B was leached with 1 N hydrochloric acid to remove the alumina debris. The zeolites were composited with alumina by comulling and then extruded. The extrudate was impregnated with the hydrogenation metals using standard procedures. The catalysts had the following characteristics:

Catalyst Zeolite	A	B	C
	Steamed Ultra- stable Y	Steamed/ Dealuminated Ultra- stable Y	Ultra- stable Y
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Wt. % Zeolite	15	15	15
Wt. % Ni	6.9	4.0	3.4
Wt. % W	17.2	21.0	20.0
10 Cell Constant, Å	24.44	24.36	24.58
SiO ₂ :Al ₂ O ₃	5:1	29:1	15:1

15 The catalysts were tested in a one-step hydrocracking process using a straight-run Arabian Light vacuum gas oil feed having the following characteristics:

°API	22.9
Aniline Pt., °F (°C)	177.5 (81°C)
S, weight percent	2.15
20 N, ppm	877
Distillation (D-1160), °C:	
St/5	339 / 374
10/30	381 / 413
25 50	448
70/90	467 / 503
95/EP	511 / 536

30 Reaction conditions included an LHSV of 1.2; 1470 psig H₂ (101 bar); and 5000 SCF/bbl feed recycle gas.

The highly desirable product characteristics produced by the process of the invention are illustrated in FIGS. 4, 5, and 6. The steamed/leached zeolite produces significantly more middistillate (FIG. 4) of lower aromatics content (FIG. 6) than the steamed and untreated Y zeolite. Additionally, cracking of the feed to naphtha-range materials occurs to a significantly lower extent (FIG. 5) with the steamed/dealuminated zeolite catalyst.

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Example 4

5 A steamed (1375°F; 746°C) Y zeolite having a silica:alumina mole ratio of 5.1:1 was washed with an approximately 1 M HCl solution (0.74 cc concentrated HCl/g zeolite). The leached product had a silica:alumina mole ratio of 9.6:1. The pore size distributions for both materials (relative pore volume $dV/d(\log d)$ as a function of pore diameter) are contrasted in FIG. 7.

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01 CLAIMS:

1. A process for selectively producing a middistillate hydrocarbon product of which more than 40 percent by volume boils above 300°F (149°C) and below 700°F

05 (371°C), which process comprises:

(a) contacting under hydrocracking conditions a hydrocarbonaceous feed boiling above 600°F (316°C) with a catalyst comprising a hydrogenation component and an expanded pore zeolite on a refractory inorganic oxide support, the zeolite being a faujasitic zeolite which has been steamed and then dealuminated, the contacting be carried out under conditions such as to produce the desired middistillate product; and

15 (b) recovering as effluent the desired middistillate product.

2. A process according to Claim 1, wherein said faujasitic zeolite is a Y zeolite.

3. A process according to Claim 2, wherein said faujasitic zeolite is an ultrastable Y zeolite having a sodium content of less than 0.5 wt. % (as Na₂O).

4. A process according to Claim 2 or 3, wherein said expanded pore zeolite has a cubic cell constant less than 24.40 Angstroms and a silica to alumina mole ratio greater than 10:1.

25 5. A process according to Claim 4, wherein said silica to alumina mole ratio is greater than 20:1.

6. A process according to any preceding claim, wherein said expanded pore zeolite contains less than 200 ppm by weight of alkali metal oxide.

30 7. A process according to any preceding claim, wherein said faujasitic zeolite is one which has been dealuminated by contacting the steamed faujasitic zeolite with an acid at a pH less than 2.

35 8. A process according to any preceding claim, wherein said faujasitic zeolite is one which has been steamed at a temperature above 1000°F (538°C).



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- 01 9. A process according to any preceding claim,
 wherein said steaming is effected with stagnant water.
10. A process according to any preceding claim,
 wherein said hydrogenation component is nickel, cobalt,
05 molybdenum, or tungsten or an oxide or sulfide thereof,
 or mixtures thereof.
11. A process according to any preceding claim,
 wherein the refractory inorganic oxide support is alumina.
12. A process according to any preceding claim,
10 wherein more than 60 percent by volume of said effluent
 boils between 400°F (204°C) and 700°F (371°C).
13. A process according to any preceding claim,
 wherein said feed is a gas oil.
14. A process according to any preceding claim and
15 further comprising at least one further hydrocracking
 step.
15. A process in accordance with Claim 1 for select-
 ively producing middistillate hydrocarbons substantially
 as described in any one of the foregoing Examples.

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