

1 **PROCESS FOR PRODUCING**
2 **HIGH RON GASOLINE USING ATS ZEOLITE**

3
4 CROSS REFERENCE TO RELATED APPLICATION

5
6 This application is related to Applicants' U.S. Patent Application Serial
7 No. 10/374,297 titled "Process For Producing High RON Gasoline Using CFI
8 Zeolite" filed February 25, 2003.

9
10 FIELD OF THE INVENTION

11
12 The invention relates to the production of high RON gasoline using
13 ATS zeolite.

14
15 BACKGROUND OF THE INVENTION

16
17 Modern automobile engines require high octane gasoline for efficient
18 operation. Previously lead had been added to gasoline to increase the octane
19 number. However, with the removal of lead from the gasoline pool due to
20 environmental concerns, other methods for increasing the octane number are
21 needed. The addition of oxygenates, such as methyl-t-butyl ether (MTBE) and
22 ethanol, may be added to gasoline to increase the octane number. However,
23 MTBE, while generally less toxic than lead, has been linked to ground water
24 contamination. At the same time, some of the high octane components
25 normally present in gasoline, such as benzene, aromatics, and olefins, must
26 also be reduced. Obviously, a process which will increase the octane of
27 gasoline without the addition of toxic or environmentally adverse substances
28 would be desirable.

29
30 For a given carbon number of a light naphtha component, the shortest, most
31 branched isomer tends to have the highest octane number. For example, the
32 branched isomers of hexane, monomethylpentane and dimethylbutane, have
33 octane numbers that are significantly higher than that of n-hexane, with
34 dimethylbutane having the highest RON. Likewise, the branched isomer of

1 pentane, methylbutane, has a significantly higher RON than n-pentane. By
2 increasing the proportion of these high octane isomers in the gasoline pool
3 satisfactory octane numbers may be achieved for gasoline without additional
4 additives. Adsorbents, such as zeolite 5A, which are selective for the least
5 bulky, lowest RON isomers are known and have been employed in
6 commercial processes following an isomerization operation in order to
7 separate the high RON isomers from the low RON isomers present in light
8 naphtha. In a different approach, U.S. Patent No. 5,107,052 describes a
9 process for increasing the octane number of gasoline by isomerizing the C₅
10 and C₆ paraffins and then selectively adsorbing the dimethylbutane using a
11 molecular sieve selected from the group consisting of AIPO₄-5, SAPO-5,
12 SSZ-24, MgAPO-5, and MAPSO-5. In each of these approaches the high
13 RON isomers recovered are added to the gasoline pool to increase the octane
14 number. The low RON isomers which are recovered separately may be
15 recycled to the isomerization operation.

16

17 Two methods for calculating octane numbers are currently being used, the
18 Motor-method octane number (MON) determined using ASTM D2700 and the
19 Research-method octane number (RON) determined using ASTM D2699. The
20 two methods both employ the standard Cooperative Fuel Research (CFR)
21 knock-test engine, but the values obtained are not identical. Sometimes the
22 MON and RON are averaged, (MON + RON)/2, to obtain an octane number.
23 Therefore, when referring to an octane number, it is essential to know which
24 method was used to obtain the number. In this disclosure, unless clearly
25 stated otherwise, octane number will refer to the RON.

1 For the purpose of comparison, the isomers of hexane and pentane have the
2 following RON's:

3		
4	n-pentane	61.7
5	methylbutane	92.3
6	n-hexane	24.8
7	2-methylpentane	73.4
8	3-methylpentane	74.5
9	2,2-dimethylbutane	91.8
10	2,3-dimethylbutane	101.0

11
12 In this disclosure, the isomers 2-methylpentane and 3-methylpentane will be
13 collectively referred to as monomethylpentane. Likewise the isomers
14 2,2-dimethylbutane and 2,3-dimethylbutane will be collectively referred to as
15 dimethylbutane. The monomethyl isomer of pentane will be referred to as
16 methylbutane. The isomers of C₅ and C₆ paraffin are included in the light
17 naphtha fraction of the gasoline pool. One skilled in the art will recognize that
18 some isomers of C₇ paraffin may also be present in the light naphtha fraction,
19 however, since heptane and its isomers are generally only present in minor
20 amounts, they will be ignored in the following discussion of the present
21 invention.

22
23 Gasoline is generally prepared from a number of blend streams. Gasoline
24 blending streams typically have a normal boiling point within the range of
25 0 degrees C (32 degrees F) and 260 degrees C (500 degrees F) as
26 determined by an ASTM D86 distillation. Feeds of this type include light
27 naphthas typically having a boiling range of from about 15 degrees C to about
28 70 degrees C (about 60 degrees F to about 160 degrees F); full range
29 naphthas, typically having a boiling range of about C₅ to 180 degrees C
30 (355 degrees F), heavier naphtha fractions boiling in the range of about
31 125 degrees C to 210 degrees C (260 degrees F to 412 degrees F), or
32 heavy gasoline fractions boiling at, or at least within, the range of about
33 165 degrees C to 260 degrees C (330 degrees F to 500 degrees F),

1 preferably from about 165 degrees C to 210 degrees C (330 degrees F to
2 412 degrees F). In general, a gasoline fuel will distill over the range of from
3 about room temperature to 260 degrees C (500 degrees F). The gasoline pool
4 typically includes butanes, light straight run, isomerase, FCC cracked
5 products, hydrocracked naphtha, coker gasoline, alkylate, reformate, added
6 ethers, etc. Of these, gasoline blend stocks from the FCC, the reformer and
7 the alkylation unit account for a major portion of the gasoline pool.
8 FCC gasoline, and if present, coker naphtha and pyrolysis gasoline, generally
9 contribute a substantial portion of the pool sulfur.

10

11 Gasoline suitable for use as fuel in an automobile engine should have a RON
12 of at least 80, preferably at least 85, and most preferably 90 or above. High
13 performance engines may require a fuel having a RON of about 100. Most
14 gasoline blending streams will have a RON ranging from about 55 to about
15 95, with the majority falling between about 80 and 90. Obviously, it is
16 desirable to maximize the amount of methylbutane and dimethylbutane in the
17 gasoline pool in order to increase the overall RON. The present invention is
18 directed to this problem.

19

20 ATS zeolites are a molecular sieve having 12-ring pores. In general ATS-type
21 zeolites include silicate-series crystalline microporous materials, such as
22 crystalline alumino-silicates, crystalline metallo-silicates, and crystalline
23 metallo-aluminosilicates having the ATS structure which is exemplified by
24 SSZ-55. SSZ-55 is described and its preparation is taught in U.S. Patent
25 No. 6,475,463 B1. This reference also teaches its use as an isomerization
26 and hydrocracking catalyst. However, the ability of SSZ-55 to preferentially
27 adsorb methylbutane and dimethylbutane as compared to the other isomers
28 of C₅ and C₆ paraffins has not been previously described and makes it
29 possible to operate isomerization and hydrocracking operations in a highly
30 efficient mode which was not recognized in the prior art.

31

32 As used in this disclosure the words "comprises" or "comprising" are intended
33 as open-ended transitions meaning the inclusion of the named elements, but

1 not necessarily excluding other unnamed elements. The phrases "consists
2 essentially of" or "consisting essentially of" are intended to mean the
3 exclusion of other elements of any essential significance to the composition.
4 The phrases "consisting of" or "consists of" are intended as transitions
5 meaning the exclusion of all but the recited elements with the exception of
6 only minor traces of impurities.

7

8

BRIEF DESCRIPTION OF THE INVENTION

9

10 In its broadest aspect the present invention is directed to a process for
11 producing a high RON naphtha which comprises contacting a hydrocarbon
12 feed stream comprising a mixture of the isomers of C₅ and C₆ paraffins with
13 ATS zeolite in an adsorption zone, whereby the branched isomers of the C₅
14 and C₆ paraffins are preferentially adsorbed by the ATS zeolite as compared
15 to the straight chain isomers, and recovering a naphtha product from the
16 adsorption zone having a higher RON than the hydrocarbon feed stream. In
17 carrying out the process the naphtha product will preferably have a RON at
18 least 2 octane numbers higher than the hydrocarbon feed stream.

19

20 The present invention is also directed to a process for isomerizing a light
21 naphtha feed stream comprising isomers of C₅ and C₆ paraffins which
22 comprises contacting the light naphtha feed stream with an ATS zeolite in a
23 hydroisomerization zone under hydroisomerization conditions, whereby the
24 isomer methylbutane is preferentially formed as compared to n-pentane and
25 the isomer dimethylbutane is preferentially formed as compared to
26 monomethylpentane and n-hexane, and recovering from the
27 hydroisomerization zone by catalytic distillation a naphtha product stream
28 enriched with methylbutane and dimethylbutane. Another embodiment of the
29 invention may be described as a process for preparing gasoline having a
30 high RON and low oxygenates which comprises contacting a hydrocarbon
31 feed stream in a hydrocracking zone with a hydrocracking catalyst under
32 hydrocracking conditions, wherein the hydrocracking catalyst comprises an
33 ATS zeolite, an active hydrocracking catalyst, and a hydrogenation

1 component, and recovering from the hydrocracking zone a methylbutane and
2 dimethylbutane enriched naphtha product.

3

4 In carrying out the process of the present invention the preferred ATS zeolite
5 is SSZ-55.

6

7 Although each of the three embodiments of the invention described above
8 involves processes which are generally treated differently in the art, it is
9 believed that the same mechanism is operative in each process. Although not
10 well understood in the art, the mechanism of the invention relates to the ability
11 of the ATS zeolite generally, and SSZ-55 in particular, to preferentially adsorb
12 methylbutane and dimethylbutane as compared to pentane,
13 monomethylpentane and n-hexane. The pores of SSZ-55 have been found to
14 admit all of the C₅ and C₆ paraffin isomers, however, the shorter chains of the
15 methylbutane and dimethylbutane are favored over the longer chains of
16 n-pentane, n-hexane and monomethylbutane. Consequently, it is possible to
17 preferentially adsorb those isomers having the highest RON. The
18 methylbutane and dimethylbutane subsequently may be recovered as part of
19 an enriched naphtha product. Preferably, the enriched naphtha product
20 should have a RON of at least 85.

21

22 When the ATS zeolite is used in a process for the simple separation of the
23 methylbutane and dimethylbutane from the other isomers of C₅ and C₆
24 paraffins, the zeolite may be employed without any active metals being
25 added. However, when using the ATS zeolite as a hydroisomerization
26 catalyst, it is usually desirable to add an active metal selected from
27 Group VIIIA of the Periodic Table of the Elements. When referring to the
28 Periodic Table of the Elements in this disclosure, the version according to the
29 1975 rules of the International Union of Pure and Applied Chemistry is the one
30 referred to herein. The preferred metals include platinum or palladium or a
31 combination of platinum and palladium. In the hydroisomerization process, the
32 methylbutane and dimethylbutane may be readily recovered from the column
33 by using catalytic distillation, since the isomers having the highest RON also

1 have a lower boiling point than the other corresponding C₅ and C₆ paraffin
2 isomers.

3

4 When the ATS zeolite is used in a hydrocracking operation, the zeolite is
5 mixed with an active hydrocracking catalyst favoring the production of
6 naphtha, such as, for example, Y-zeolite. Although the ATS zeolite may have
7 some cracking activity of its own, its primary purpose in the cracking operation
8 is to adsorb the C₅ and C₆ paraffin isomers present in the hydrocracking zone.
9 In addition, the SSZ-55 will preferentially isomerize the n-pentane to
10 methylbutane and isomerize the n-hexane and monomethylpentane to
11 dimethylbutane which will further increase the RON of the effluent from the
12 hydrocracking operation. Thus by including the ATS zeolite in the
13 hydrocracking catalyst, a methylbutane and dimethylbutane enriched naphtha
14 product can be recovered which may be used to prepare gasoline having an
15 acceptable RON without the addition of oxygenates. The mixture of the
16 ATS zeolite and cracking catalyst preferably will also contain a hydrogenation
17 component, such as an active metal selected from Group VIIIA and/or
18 Group VIB of the periodic Table of the Elements.

19

20 When the process of the invention is being used as part of a simple
21 separation operation to recover the methylbutane and dimethylbutane from
22 the hydrocarbon feed stream or when the process is being used as part of a
23 hydroisomerization operation, the feed stream preferably will be a light
24 naphtha stream in order to minimize the volume of material passing through
25 the operation. When the process is being employed in a hydrocracking
26 operation heavier feeds would obviously be employed which are cracked into
27 products boiling in the range of naphtha. Although the ATS zeolite may be
28 used in either a single stage or two stage hydrocracking operation, the
29 ATS zeolite is most advantageously employed in the second stage of a
30 two-stage hydrocracking operation in order to minimize coking of the catalyst.

1 DETAILED DESCRIPTION OF THE INVENTION

2

3 In this disclosure the terms ATS type zeolite, ATS molecular sieve, or
4 variations thereof refers to the framework structure code for a family of
5 molecular sieve materials which are exemplified by the zeolite SSZ-55. The
6 Structure Commission of the International Zeolite Association (IZA) gives
7 codes consisting of three alphabetical letters to zeolites (molecular sieves)
8 having a structure that has been determined. Zeolites having the same
9 topology are generically called by such three letters. Molecular sieves
10 included within the code ATS include SSZ-55, MAPO-36, CoAPO-36,
11 MnAPO-36, ZAPO-36, FCAPO-36, XAPO-36, and ZnAPSO-36. Thus zeolites
12 having a framework structure similar to that for SSZ-55 are named an
13 ATS-type zeolite. The parameters of ATS type molecular sieves is further
14 described in the *Atlas of Molecular Sieves* which is published by the IZA
15 following the rules set up by an IUPAC Commission on Zeolite Nomenclature
16 in 1978.

17

18 In general, ATS-type zeolites refer to silicate-series crystalline microporous
19 materials, which include SAPO's, MAPO's, ALPO's, crystalline
20 alumino-silicates, crystalline metallo-silicates, and crystalline
21 metallo-aluminosilicates having the ATS structure. Metallo-silicates and
22 metallo-aluminosilicates mean herein aluminosilicates, part or all of aluminum
23 therein are replaced with other metals than aluminum, other metals which
24 include gallium, iron, titanium, boron, cobalt, and chromium. Elements forming
25 the framework structure other than silicon and oxygen, for example,
26 aluminum, gallium, iron, titanium, boron, cobalt, zinc, magnesium, and
27 chromium are herein defined as heteroatoms.

28

29 The zeolite SSZ-55 which represents a preferred catalyst for use in the
30 process of the invention is described in U.S. Patent No. 6,475,463 which is
31 incorporated herein in its entirety. MAPO-36 is described in *Zeolites*, 13,
32 166-169 (1993). Of the other ATS zeolites, ZAPO-36 is described in
33 U.S. Patent No. 4,567,029, ZnAPSO-36 in U.S. Patent No. 4,793,984,

1 FCAPO-36 in U.S. Patent No. 4,686,093, XAPO-36 in U.S. Patent
 2 No. 4,952,384 and CoAPO-36 in U.S. Patent No. 4,567,029, all of which are
 3 incorporated by reference in their entirety.
 4
 5 SSZ-55 is a zeolite, silica or a substituted aluminum phosphate having a
 6 12 atom pore structure. The zeolite is described as having a mole ratio
 7 greater than two of an oxide of a first tetravalent element to an oxide of a
 8 second tetravalent element different from the first tetravalent element, trivalent
 9 element, pentavalent element, or mixture thereof. As noted above, its
 10 preparation and characteristics are more fully described in U.S. Patent
 11 No. 6,475,463. In general, the zeolite is a molecular sieve which may be
 12 obtained in a variety of forms, including, for example, silicate, aluminosilicate,
 13 titanosilicate, vanadosilicate, or borosilicate forms. Substituted aluminum
 14 phosphates include metal- and silicon-substituted sieves such as MgAPO-36,
 15 MAPO-36, and MAPSO-36. The term "silicate" refers to a zeolite having a
 16 high mole ratio of silicon oxide relative to aluminum oxide, preferably a mole
 17 ration greater than 400. As used herein the term "aluminosilicate" refers to a
 18 zeolite containing both alumina and silica. The term "borosilicate" refers to a
 19 zeolite containing oxides of both boron and silicon. Representative X-ray
 20 diffraction lines for the as-synthesized zeolite are shown in Table I and for the
 21 zeolite after calcination are shown in Table II.

TABLE I

2-Theta ^(a)	As-synthesized SSZ-55	Relative Intensity ^(b)
7.94	11.13	S
15.98	5.54	M
16.60	5.33	S
19.24	4.61	M
20.97	4.23	VS
21.93	4.05	M
22.48	3.95	VS
23.68	3.75	M
27.54	3.24	M
35.08	2.56	W

^(a) ± 0.02

^(b) The X-ray patterns provided are based on a relative intensity scale in which the strongest line in the X-ray pattern is assigned a value of 100; W (weak) is less than 20; M (medium) is between 20 and 40; S (strong) is between 40 and 60; VS (very strong) is greater than 60.

TABLE II

2-Theta ^(a)	Calced SSZ-55 d	Relative Intensity ^(b)
7.94	11.13	VS
13.60	6.51	W
16.67	8.31	M
19.31	4.59	WM
20.92	4.24	WM
22.00	4.04	W
22.56	3.94	WM
27.46	3.24	W
28.73	3.10	W
32.32	2.77	W

The X-ray powder diffraction patterns were determined by standard techniques which are described in detail in U.S. Patent No. 6,475,463 B1.

As noted above, the pores of SSZ-55 will admit all of the isomers of n-pentane and n-hexane, however, the more compact isomers, which include methylbutane, 2,3-dimethylbutane, and 2,2-dimethylbutane, are preferentially adsorbed. While not wishing the invention to be bound by any particular theory as to why methylbutane and the two dimethylbutane isomers are preferentially adsorbed, it may be helpful to briefly discuss what is believed to be the mechanism involved. It is speculated that the methylbutane and dimethylbutane isomers being more compact than n-pentane, n-hexane, or monomethylpentane are preferentially adsorbed as a result of entropy. See Understanding Zeolite Catalysis; Inverse Shape Selectivity Revisited by Merijn Schenck, et al., Agnew. Chem. Int. Ed. 2002, No. 14, pgs. 2499-2502. According to this theory, the shorter, more compact molecules may be more efficiently packed into the pores of the zeolite than the longer molecules. Accordingly, the more compact molecules when present in sufficient concentration will displace the longer chain molecules.

The preferential adsorption of methylbutane and dimethylbutane may be used as an efficient means for their separation from the other C₅ and C₆ paraffin isomers. When a hydrocarbon stream containing the various isomers of pentane and hexane are passed over a catalyst bed comprising SSZ-55, the SSZ-55 will preferentially adsorb the methylbutane and dimethylbutane. The

1 phrase "preferentially adsorb" implies that while all of the isomers of pentane
2 and hexane will be adsorbed, the methylbutane and dimethylbutane will be
3 preferred if they are present in sufficient concentration to displace the other
4 isomers. Thus the pores in the zeolite will become saturated with the
5 preferred isomers if they are presented in sufficient concentration. Although
6 the adsorption of the favored isomers will proceed over a wide range of
7 temperatures and pressures, it has been observed that the adsorptive
8 efficiency of the zeolite in separating the favored isomers generally improves
9 as the temperature and pressure increases. Therefore, it is usually desirable
10 to operate at the highest temperature and pressure which is practical from a
11 technical and economic perspective.

12

13 U.S. Patent No. 5,107,052 describes a three step process for producing a
14 high octane fuel in which the first step is an isomerization reaction where the
15 C₄ to C₆ paraffins are isomerized, the second step involves the selective
16 adsorption of the branched chain isomers from the isomerate by a molecular
17 sieve selected from the group of SAPO-5, AlPO₄-5, SSZ-24, MgAPO-5, and
18 MAPSO-5, and the final step consists of the desorption of the higher octane
19 isomers using a desorbent. While an ATS zeolite generally, and SSZ-55 in
20 particular, may be substituted as an adsorbent for the catalysts that are
21 disclosed in this reference, it has been found that by using the unique
22 properties of the ATS zeolite it is possible to efficiently recover the
23 methylbutane and dimethylbutane from the zeolite by the use of catalytic
24 distillation. By using catalytic distillation to recover the dimethylbutane, the
25 recovery operation may be performed in the same vessel as the
26 hydroisomerization and separation steps. Thus not only is the isomerization
27 operation reduced from three steps to two steps but the number of vessels
28 required can be reduced to one by use of the process of the present
29 invention. This significantly lowers the capital and operating costs of the
30 isomerization and separation operation.

31

32 In one embodiment of the present invention, the C₅ and C₆ paraffins are
33 selectively isomerized to methylbutane and dimethylbutane, respectively,

1 using ATS zeolite as the hydroisomerization catalyst. The ATS zeolite may be
2 used in the process without an active metal being present on the zeolite, but it
3 is generally preferred that the catalyst contain an effective hydroisomerization
4 amount of one or more active metals selected from Group VIIIA of the
5 Periodic Table of the Elements. Group VIIIA includes the noble metals
6 platinum, palladium, and iridium. Particularly preferred for use as the active
7 metal are platinum, palladium or a mixture of platinum and palladium. The
8 active metal is generally placed on the zeolite as a compound of the metal
9 using methods which are well known in the art. As used herein the term an
10 "effective hydroisomerization amount" refers to that loading of active metal on
11 the catalyst which is effective to isomerize the paraffins under the conditions
12 present in the hydroisomerization zone. Generally the amount of metal present
13 will exceed 0.01 weight percent metal, and preferably will fall within the range
14 from about 0.1 to about 1.0 weight percent.

15

16 In carrying out the isomerization process, the hydrocarbon feed is preferably
17 light naphtha in order to minimize the amount of feed passing through the
18 hydroisomerization zone. Since olefins, sulfur, nitrogen, and water tend to
19 deactivate the catalyst, it is generally desirable to reduce the amount of these
20 contaminants in the feed prior to their contacting the hydroisomerization
21 catalyst. The isomerization reaction is carried out in the presence of
22 hydrogen. Typically this process operates at temperatures above about
23 465 degrees F (about 240 degrees C), 30 bars, and hydrogen to hydrocarbon
24 ratio of about 2.5.

25

26 Catalytic distillation is a method for separating the methybutane and
27 dimethylbutane from the other C₅ and C₆ paraffins after they have been
28 adsorbed by the ATS zeolite using the same vessel. A general description of
29 the catalytic distillation process may be found in More uses for catalytic
30 distillation by G. G. Podrebarac, et al. in Chemtech, May, 197, pgs. 37-45.
31 Catalytic distillation is particularly useful for the separation of the high RON
32 isomers following hydroisomerization, since they have a lower boiling point
33 than the longer chain isomers which have a lower RON. Note the boiling

1 points given in degrees C for each of the isomers of C₅ and C₆ paraffins
2 listed below:

3

4 n-pentane 36.1

5 methylbutane 27.9

6 n-hexane 68.7

7 2-methylpentane 60.3

8 3-methylpentane 63.3

9 2,2-dimethylbutane 49.7

10 2,3-dimethylbutane 58.0

11

12 It should be noted that those isomers having the highest RON also display
13 significantly lower boiling points than the isomers of those paraffins having the
14 same number of carbon atoms and the lower RON. During the
15 hydroisomerization reaction, the reactor is maintained at a temperature
16 equivalent to the boiling point of the liquid in the column. Since the boiling
17 point of the liquid in the column may vary depending on the pressure in the
18 reactor, there is some flexibility in the temperature at which the reactor must
19 be maintained. In catalytic distillation, the lowest boiling liquid in the column
20 may be separated from the other liquids present having a higher boiling point.
21 For example, in the process of the present invention, the dimethylbutane has
22 a lower boiling point than the other isomers of C₆ paraffin, therefore, it is
23 relatively easy to recover the dimethylbutane by simply distilling off the lower
24 boiling material in the column. The same principle holds true for separating
25 methylbutane from n-pentane. Mixtures containing isomers of both C₅ and C₆
26 paraffins may be separated by successively distilling off the lowest boiling
27 liquids.

28

29 When employed in a hydrocracking operation, the ATS zeolite is employed in
30 combination with a conventional hydrocracking catalyst suitable for
31 maximizing the production of naphtha, such as, for example, Y-zeolite. The
32 cracking catalyst should also have a hydrogenation component such as an
33 effective amount of a Group VIIIA or Group VIB metal. As used herein an

1 effective hydrocracking amount of the active metal refers to the amount of
2 metal loaded onto the catalyst to catalyze the cracking reaction under the
3 conditions present in the hydrocracking zone. The cracking reaction is carried
4 out in the presence of free hydrogen. Typical hydrocracking conditions include
5 an overall LHSV of about 0.1 hr⁻¹ to about 15.0 hr⁻¹ (v/v), preferably from
6 about 0.25 hr⁻¹ to about 2.5 hr⁻¹. The reaction pressure generally ranges
7 from about 500 psig to about 3500 psig (about 10.4 MPa to about 24.2 MPa,
8 preferably from about 1500 psig to about 5000 psig (about 3.5 MPa to about
9 34.5 MPa). Hydrogen consumption is typically from about 500 to about
10 2500 SCF per barrel of feed (89.1 to 445 m³ H₂/m³ feed). Temperatures in
11 the reactor will range from about 400 degrees F to about 950 degrees F
12 (about 205 degrees C to about 510 degrees C), preferably ranging from about
13 650 degrees F to about 850 degrees F (about 340 degrees C to about
14 455 degrees C).

15

16 As noted earlier, the ATS zeolite, while having some cracking activity of its
17 own, is primarily intended in this embodiment of the invention to isomerize the
18 C₅ and C₆ paraffins either already present in the feed or produced by the
19 cracking of the feedstock. Accordingly, the ATS zeolite will preferably contain
20 an effective hydroisomerization amount of a Group VIIIA metal, preferably
21 platinum or palladium or a combination of platinum and palladium. While the
22 SSZ-55 may be used in the hydrocracking reactor of a single stage
23 hydrocracking operation, it is more advantageous to use the ATS zeolite in
24 the second stage of a two-stage hydrocracking operation. Use in the second
25 stage will slow the coking of the catalyst and prolong its useful life.

26

27 A two-stage hydrocracking operation contains two hydrocracking zones in
28 which the hydrocrackate or effluent from the first hydrocracking zone is
29 passed to the second hydrocracking zone. In this configuration, the first stage
30 usually will remove most of the contaminants present in the feed stock
31 allowing for the use of more contaminant sensitive catalysts in the
32 second stage. In addition, gaseous by-products, such as hydrogen sulfide and
33 ammonia, are preferably removed from the effluent prior to its introduction into

1 the second stage. Two-stage hydrocracking operations may utilize
2 two separate reactor vessels or use a single vessel in which the first stage
3 and second stage catalysts are "stacked" in the reactor vessel.

4
5 Suitable hydrocracking catalysts which may be mixed with the SSZ-55 are
6 well known in the art. See for example U.S. Patent Nos. 4,347,121 and
7 4,810,357, the contents of which are hereby incorporated by reference in their
8 entirety, for general descriptions of typical hydrocracking catalysts. Suitable
9 hydrocracking catalysts include noble metals from Group VIIIA, such as
10 platinum or palladium on an alumina or siliceous matrix, and Group VIB
11 metals, such as nickel-molybdenum or nickel-tin on an alumina or siliceous
12 matrix. The non-noble hydrogenation metals, such as nickel-molybdenum, are
13 usually present in the final catalyst composition as oxides, but are usually
14 employed in their reduced or sulfided forms when such sulfide compounds are
15 readily formed from the particular metal involved. Preferred non-noble metal
16 catalyst compositions contain in excess of about 5 weight percent, preferably
17 about 5 to about 40 weight percent molybdenum and/or tungsten, and at least
18 about 0.5, and generally about 1 to about 15 weight percent of nickel and/or
19 cobalt determined as the corresponding oxides. Catalysts containing noble
20 metals, such as platinum, contain in excess of 0.01 percent metal, preferably
21 between about 0.1 weight percent and about 1.0 weight percent metal.
22 Combinations of noble metals may also be used, such as mixtures of platinum
23 and palladium.

24
25 The hydrogenation components can be incorporated into the overall
26 hydrocracking catalyst composition by any one of numerous procedures. The
27 hydrogenation components can be added to matrix component by co-mulling,
28 impregnation, or ion exchange and the Group VIB components,
29 i.e.; molybdenum and tungsten can be combined with the refractory oxide by
30 impregnation, co-mulling or co-precipitation.

31
32 The matrix component for the hydrocracking catalyst can be of many types
33 including some that have acidic catalytic activity. Ones that have activity

1 include amorphous silica-alumina or zeolitic or non-zeolitic crystalline
2 molecular sieves. Examples of suitable matrix molecular sieves include zeolite
3 Y, zeolite X and the so called ultra stable zeolite Y and high structural
4 silica-alumina ratio zeolite Y such as that described in U.S. Patent
5 Nos. 4,401,556; 4,820,402; and 5,059,567. Small crystal size zeolite Y, such
6 as that described in U.S. Patent No. 5,073,530 can also be used. Non-zeolitic
7 molecular sieves which can be used include, for example,
8 silicoaluminophosphates (SAPO), ferroaluminophosphate, titanium
9 aluminophosphate and the various ELAPO molecular sieves described in
10 U.S. Patent No. 4,913,799 and the references cited therein. Details regarding
11 the preparation of various non-zeolite molecular sieves can be found in
12 U.S. Patent Nos. 5,114,563 (SAPO) and 4,913,799 and the various
13 references cited in U.S. Patent No. 4,913,799. Mesoporous molecular sieves
14 can also be used, for example the M41S family of materials as described in
15 J. Am. Chem. Soc., 114:10834-10843(1992)), MCM-41;
16 U.S. Patent Nos. 5,246,689; 5,198,203; and 5,334,368; and MCM-48
17 (Kresge et al., Nature 359:710 (1992)). Suitable matrix materials may also
18 include synthetic or natural substances as well as inorganic materials such as
19 clay, silica and/or metal oxides such as silica-alumina, silica-magnesia,
20 silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary
21 compositions, such as silica-alumina-thoria, silica-alumina-zirconia,
22 silica-alumina-magnesia, and silica-magnesia zirconia. The latter may be
23 either naturally occurring or in the form of gelatinous precipitates or gels
24 including mixtures of silica and metal oxides. Naturally occurring clays which
25 can be composited with the catalyst include those of the montmorillonite and
26 kaolin families. These clays can be used in the raw state as originally mined
27 or initially subjected to dealumination, acid treatment or chemical modification.
28
29 In carrying out the present invention, those hydrocracking catalyst which
30 maximizes the production of naphtha, particularly light naphtha are preferred.
31 Thus acidic hydrocracking catalysts, such as, for example, Y-zeolites, are
32 particularly preferred for admixture with the ATS zeolite.

1 WHAT IS CLAIMED IS:

2

3 1. A process for producing a high RON naphtha which comprises contacting
4 a hydrocarbon feed stream comprising a mixture of the isomers of C₅ and
5 C₆ paraffins with ATS zeolite in an adsorption zone, whereby the branched
6 isomers of the C₅ and C₆ paraffins are preferentially adsorbed by the ATS
7 zeolite as compared to the straight chain isomers, and recovering a
8 naphtha product from the adsorption zone having a higher RON than the
9 hydrocarbon feed stream.

10

11 2. The process of claim 1 wherein the hydrocarbon feed stream is light
12 naphtha.

13

14 3. The process of claim 2 wherein the RON of the naphtha product is
15 increased by at least 2 octane numbers as compared to the light naphtha
16 feed stream.

17

18 4. The process of claim 2 wherein the adsorption zone is maintained under
19 hydroisomerization conditions and the ATS zeolite also serves as a
20 hydroisomerization catalyst to selectively isomerize pentane to
21 methylbutane and isomerize monomethylpentane and n-hexane to
22 dimethylbutane.

23

24 5. The process of claim 4 wherein the naphtha product has a RON of at least
25 85.

26

27 6. The process of claim 1 wherein the adsorption zone is maintained under
28 hydrocracking condition and the ATS zeolite is one component of a
29 hydrocracking catalyst system comprising the ATS zeolite, an active
30 hydrocracking catalyst, and an effective amount of a hydrogenation
31 component.

1

2 7. The process of claim 1 wherein the ATS zeolite is selected from one or
3 more of SSZ-55, MAPO-36, CoAPO-36, MnAPO-36, ZAPO-36, FCAPO-
4 36, XAPO-36, and ZnAPSO-36.

5

6 8. The process of claim 7 wherein the ATS zeolite is SSZ-55

7

8 9. A process for isomerizing a light naphtha feed stream comprising isomers
9 of C₅ and C₆ paraffins which comprises contacting the light naphtha feed
10 stream with an ATS zeolite in a hydroisomerization zone under
11 hydroisomerization conditions, whereby the isomer methylbutane is
12 preferentially formed as compared to n-pentane and the isomer
13 dimethylbutane is preferentially formed as compared to
14 monomethylpentane and n-hexane, and recovering from the
15 hydroisomerization zone by catalytic distillation a naphtha product stream
16 enriched with methylbutane and dimethylbutane.

17

18 10. The process of claim 9 wherein the ATS zeolite is selected from one or
19 more of SSZ-55, MAPO-36, CoAPO-36, MnAPO-36, ZAPO-36, FCAPO-
20 36, XAPO-36, and ZnAPSO-36.

21

22 11. The process of claim 10 wherein the ATS zeolite is SSZ-55.

23

24 12. The process of claim 11 wherein the SSZ-55 contains an effective amount
25 of at least one active metal selected from Group VIIIA of the Periodic
26 Table of the Elements.

27

28 13. The process of claim 12 wherein the active metal is selected from one of
29 platinum, palladium, or a combination of platinum and palladium.

30

- 1 14. A process for preparing gasoline having a high RON and low oxygenates
2 which comprises contacting a hydrocarbon feed stream in a hydrocracking
3 zone with a hydrocracking catalyst under hydrocracking conditions,
4 wherein the hydrocracking catalyst comprises an ATS zeolite, an active
5 hydrocracking catalyst, and a hydrogenation component, and recovering
6 from the hydrocracking zone a methylbutane and dimethylbutane enriched
7 naphtha product.
8
- 9 15. The process of claim 14 wherein the process includes a first
10 hydrocracking zone and a second hydrocracking zone wherein the effluent
11 from the first hydrocracking zone is passed to the second hydrocracking
12 zone and the hydrocracking catalyst containing the ATS zeolite is in the
13 second hydrocracking zone.
14
- 15 16. The process of claim 14 wherein the ATS zeolite is selected from one or
16 more of SSZ-55, MAPO-36, CoAPO-36, MnAPO-36, ZAPO-36, FCAPO-
17 36, XAPO-36, and ZnAPSO-36.
18
- 19 17. The process of claim 16 wherein the ATS zeolite is SSZ-55.
20
- 21 18. The process of claim 14 wherein the ATS zeolite contains a hydrogenation
22 component which comprises at least one active metal selected from
23 Group VIIIA or Group VIB of the Periodic Table of the Elements.
24
- 25 19. The process of claim 14 wherein the dimethylbutane and methylbutane
26 enriched naphtha product has a RON of at least 90.
27