

Process for the treatment of olefinic gasoline

This invention relates to the treatment of highly olefinic gasoline containing at least about 50% by weight of olefins by contacting said olefinic gasoline with an acidic crystalline aluminosilicate zeolite, for example of the ZSM-5 type, in order to enhance the gum stability of said gasoline and produce products comprising both gasoline and fuel oil.

5 There are many processes known in the patent and technical literature which produce olefinic gasolines having an olefin content of at least 50 weight percent. One such process, described in US-A-3,960,978, involves the conversion of gaseous C_2-C_8 olefins to an olefinic gasoline by passage over a ZSM-5 type catalyst of controlled acidity. Thus, by way of illustration, a light olefin product stream produced by fluid catalytic cracking processes is charged over ZSM-5 as "wet" gas and results in
10 olefinic gasoline. The "wet" gas comes from a piece of equipment called an accumulator which is upstream of the gas plant compressor. A more recent process resulting in the production of olefinic gasolines involves contacting synthesis gas over iron or cobalt ZSM-5 type compositions under certain conditions. This process is believed to go through a light olefin intermediate (*Journal of Catalysis*, Vol. 56, 274, 1979).

15 These olefinic gasolines have good unleaded research octane numbers of 90 and higher, but unfortunately also have poor gum stability. In addition, reaction constraints in both systems, i.e. the petroleum route and the synthesis gas route, limit the liquid product essentially to gasoline. In some situations, especially in those areas of the world that are short of petroleum, the synthesis gas route might be attractive and it would be advantageous to produce both gasoline and fuel oil products such
20 as diesel fuel, home heating oils, jet fuel, etc.

It is to be specifically noted that the broad concept of contacting an olefinic charge with the class of zeolites with which this invention is concerned is known in the art and is the subject of various United States patents. Thus, for example, US-A-3,960,978 teaches conversion of olefins to olefinic gasolines. US-A-4,021,502 discloses conversion of olefins over ZSM-12. US-A-3,760,024 discloses
25 contacting olefins with ZSM-5 type zeolites. US-A-3,778,501 discloses preparation of aromatics by contacting olefins over ZSM-5 type catalysts. US-A-3,827,968 discloses a two-step aromatization process wherein in the first step an olefin is contacted over a ZSM-5 type zeolite. US-A-3,845,150 discloses contacting a feed comprising saturated and unsaturated compounds over a ZSM-5 type zeolite in order to form aromatics. US-A-3,843,740 also discloses an aromatization process wherein
30 various feed streams, including gasoline are contacted with ZSM-5 type zeolites. US-A-3,756,942 discloses an aromatization process involving contact over ZSM-5 type catalysts of various feeds, including gasoline. However, none of the prior art is directed towards the concept of treating olefinic gasoline at relatively mild reaction conditions with a ZSM-5 type zeolite to yield reaction products comprising both fuel oil and gasoline, said gasoline having enhanced gum stability.

35 The novel process of this invention is directed towards contacting an olefinic gasoline containing at least about 50 weight percent of olefins with a class of zeolites under very specific reaction conditions so as to selectively react olefins and produce both gasoline and fuel oil.

The crystalline aluminosilicate zeolites utilized herein are members of a class of zeolites that exhibits unusual properties.

40 Briefly, the preferred type zeolites useful in this invention possess, in combination: a silica to alumina mole ratio of at least about 12; a dried crystal density of not less than about 1.6 grams per cubic centimeter and a constraint index of about 1 to about 12. Crystal density, constraint index and the measurement thereof are described in US-A-4,118,431.

An important characteristic of the crystal structure of this class of zeolites is that it provides
45 constrained access to and egress from the intracrystalline free space by virtue of having an effective pore size intermediate the small pore Linde A and the large pore Linde X.

Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e. they exhibit
50 "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38, defined respectively by the X-ray diffraction data presented in US-A-3,702,886, 3,709,979, 3,822,449, 4,016,245 and 4,046,859. The preferred zeolite is ZSM-5. The zeolites may be utilized in
55 the hydrogen form or they may be stabilized with rare earth or other metal cations.

In practicing the desired conversion process, it may be desirable to incorporate the above described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides.

60 As has heretofore been stated, the broad concept of contacting olefins, including olefinic gasoline over the identical catalyst with which this invention is concerned is not per se novel. The entire key to

the inventive concept of this invention resides in choosing a certain limited critical range of operating conditions such that the following three objectives will be accomplished:

- (1) Gasoline having improved gum stability will be obtained;
- (2) substantially no aromatics will be made, i.e. a net increase of less than 5 weight percent; and
- (3) the products obtained will comprise both fuel oil and gasoline.

The general operating parameters for carrying out the novel process of this invention can be defined by stating that the process is carried out at pressures from about 790 kPa (100 psig) to 7000 kPa (1000 psig) at temperatures ranging from 177°C (350°F) to 316°C (600°F) and at space velocities of 0.2 to 10 LHSV. It is to be immediately understood that the above recitation of ranges of pressure, space velocity, and temperature is not intended to mean that all operations within the above set forth limits will result in producing the desired results of the instant invention. On the contrary, what is meant by the above limits concerning temperature, pressure and space velocity is best expressed in a negative way. Operations outside the ranges specifically set forth will not result in the improved process of this invention. It is well known in the art that there is a correlation between temperature, pressure and space velocity with respect to the severity of a given chemical reaction. Quite simply put, the instant invention is concerned with conversion of the most active gum forming olefins to fuel oil (probably via polymerization) at a severity such that non-gum forming olefins, such as highly branched olefins are substantially unaffected. A net production of aromatics, i.e. greater than 5 weight percent, is contrary to the above objective.

One way of ascertaining whether or not the correct severity is being utilized is by reference to the C_6+ liquid yield. In the novel process of this invention, the C_6+ liquid yield of the product obtained should not be any more than 5 volume percent less than the C_6+ liquid yield of the starting gasoline, i.e. it should be at least 95%.

Thus, by way of specific illustration, reference is made to Example 13 which describes the conversion of an olefinic gasoline over HZSM-5 at a pressure of 4928 kPa (700 psig), a liquid hourly space velocity of 0.5 and at an average temperature of 290°C (554°F). As will be obvious, the temperature, pressure and space velocity of this example are within the broad ranges of pressure, temperature and space velocity previously set forth. However, it will be seen that the C_6+ liquid yield in this example was 74.8 volume percent, whereas the C_6+ liquid of the starting charge stock was 84.5 volume percent. Thus, the C_6+ liquid yield of Example 13 was 11.5 volume percent less than the C_6+ liquid yield of the charge stock. Therefore, the operations of this example are at a severity outside the scope of this invention. If one were desirous of operating at the pressure and temperature specified in Example 13, then one would have to increase the space velocity from 0.5 LHSV up to a point where the liquid yield obtained would be no more than 5 volume percent less than that of the charge stock. This is precisely because it is well known in the art that at a constant temperature and pressure increasing the space velocity decreases the severity of reaction. It is also known in the art that if the pressure and space velocity remain constant, then decreasing the temperature reduces the severity. Thus, again with specific reference to Example 13, as opposed to increasing the space velocity, the maximum temperature of this example should be decreased down to the point where the liquid yield obtained is no more than 5 volume percent less than the C_6+ liquid yield of the charge stock.

Thus, it is not possible to define the operating parameters of this invention merely by reciting a range of temperatures, pressures and space velocities. It is also necessary to state that within the range of pressure, temperature and space velocity a severity must be achieved which results in the net production of no more than 5 weight percent aromatics or results in a C_6+ liquid which is no more than 5 volume percent less than the charge.

Example 1 Catalyst Preparation

The HZSM-5 zeolite catalyst used in the examples was prepared by mixing a dried as synthesized ZSM-5 zeolite having a silica-alumina ratio of about 70 with alumina and water, extruding into 1.6 mm (1/16") diameter pellets. The extruded material contained 35 or 65 parts ZSM-5 per 65 or 35 parts alumina.

The dried extrudate was calcined for three hours at 538°C in flowing nitrogen. After cooling, the extrudate was contacted with an ammonium nitrate exchange solution (about 0.13 kg NH_4NO_3 /kg extrudate) for one hour at ambient temperature. This exchange was then repeated until the sodium level was less than 0.05 weight percent. The extrudate was then washed, dried and calcined in flowing air at 538°C for three hours. The extrudate was then sized to 30—60 mesh.

Example 2

A mixture of propylene/propane 63.5/36.5 weight percent was charged to a pilot plant over HZSM-5 extrudate catalyst containing 65% ZSM-5 at 1135 kPa (150 psig), 1.9 LHSV (olefin), recycle ratio 4.2 mols/mol, reactor inlet temperature 246—303°C (476—578°F), outlet 328—368°C (621—693°F) for 7 days. Propylene conversion was 95%. The average C_5+ octane number (R+O) for the 2—7 day period was 92, with C_6+ composition as follows:

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	Paraffins, total	8
	Iso	6
5	Normal	2
	Olefins	90
10	Naphthenes	1
	Aromatics	1
		100%

Example 3—7

The liquid product from Example 2, composed of 1% butenes, 7% pentenes, and 91% C₆+ material, was charged over the extruded catalyst of Example 1 containing 35% ZSM-5 at 446—6996 kPa (50—1000 psig), 232—271°C (450—520°F), ~1 LHSV, for 4 1/2 days.

The results obtained as well as the actual experimental conditions are shown in the following table:

TABLE						
Example		3	4	5	6	7
25 LHSV	C	1.0	1.1	1.0	0.9	1.0
WHSV		1.2	1.4	1.2	1.2	1.3
30 Temp. °C, Average	H	232	262	262	264	263
Maximum		233	270	271	274	269
Run Time, Hours	A	24	22	23	17	20
35 Accumulative Time, Days	R	1.0	1.9	22.9	3.6	4.4
Pressure, kPa	G	4928	4928	2859	6996	446
Liquid Product	E					
40 Gravity, °API	61.9	55.0	52.1	52.8	53.1	59.9
Yield, Wt. %						
45 C ₁ +C ₂	—	<0.1	<0.1	<0.1	<0.1	<0.1
C ₃	0.5	0.9	0.9	0.8	0.5	0.3
C ₃ =	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
50 i-C ₄	0.1	0.3	0.5	0.4	0.3	0.2
n-C ₄	0.1	0.2	0.2	0.1	0.1	0.1
C ₄ =	0.9	0.2	0.3	0.4	0.2	1.1
55 i-C ₅	0.6	1.0	1.8	1.3	1.2	0.7
n-C ₅	0.3	0.4	0.7	0.4	0.4	0.3
60 C ₅ =	6.6	2.3	1.3	1.6	1.6	6.6
C ₆ +	90.9	94.7	94.3	94.8	95.7	90.7
	100.0	100.0	100.0	100.0	100.0	100.0

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TABLE (continued)

Example		3		4		5		6		7	
Liquid Product Boiling Range, °C (°F)		70°C (159°F)		85°C (186°F)		77°C (170°F)		75°C (167°F)		53°C (128°F)	
10%	43°C (110°F)	104 (220)		127 (261)		121 (250)		119 (245)		85 (185)	
30	86 (187)	136 (278)		158 (317)		150 (301)		147 (297)		107 (226)	
50	110 (230)	163 (325)		185 (365)		181 (357)		178 (352)		136 (278)	
70	138 (281)	196 (386)		212 (414)		210 (410)		207 (406)		175 (347)	
90	171 (339)	206 (403)		220 (428)		219 (426)		217 (423)		189 (371)	
95	185 (365)	213 (415)		225 (437)		224 (436)		223 (433)		199 (390)	
98	194 (382)										
% Boiling Above 166°C (330°F)		28		44		39		38		13	
% Boiling Above 193°C (380°F)		12		24		21		20		3	
Octane Number R+O		86.2		—		—		—		91.3	

From the above table, it can be seen that pressures above about 446 kPa (50 psig) are necessary to convert the charge to fuel oil product, but there is no advantage to going above about 4928 kPa (700 psig), where the charge is already essentially all liquid phase.

Liquid products from Examples 4, 5 and 6 were composited and distilled, cut point 166°C (330°F). The 47 volume percent gasoline product boiling below 166°C (330°F) had the following properties:

10	Gravity, °API	61.7	
	Specific	0.7324	
	Boiling Range, °C (°F)		
15	10%	64°C	(147°F)
	20%	87	(189)
	50%	123	(254)
20	70%	140	(284)
	90%	163	(325)
	95%	173	(344)
25	98%	185	(366)
	Composition, Wt. %		
30	Paraffins, Total	22	
	Iso		18
	Normal		4
	Olefins	73	
35	Naphthenes	1	
	Aromatics	4	
		100%	
40	Octane No., R+O	92.4	

The 53 Vol.% 166°C+ (330°F+) product had the following properties:

45	Gravity, °API	45.4
	Specific	0.7999
	Boiling Range, °C (°F)	
50	10%	168°C (334°F)
	20%	183 (361)
	50%	217 (421)
55	70%	242 (469)
	90%	292 (558)
60	95%	322 (611)
	98%	350 (662)

0020017

Pour Point, °C <-56.7 (<-70°F)

Aniline No. °C 62 (143.0°F)

Diesel Index	65
Mol. Wt., Est.	180
Bromine No.	86.9
Calc. Double Bonds/Molecule	1.0
Hydrogen, Wt. %	13.63
Carbon, Wt. %	85.04
H/C Ratio	1.91

It can be seen that the gasoline product contained considerably less olefins than the charge, more iso-paraffins and aromatics, and about the same octane No. The 166°C+ (330°F+) fuel oil has very low pour point, high diesel index, and analyses indicating it to be essentially all aliphatic olefins.

It is to be specifically noted that the above data illustrate that substantially no net production of aromatics has occurred even though the gasoline fraction contained more aromatics than the charge. Thus, for example, the charge had an aromatic content of about 1 weight percent, i.e. see Example 2; whereas the gasoline fraction had an aromatic content of 4%. However, the gasoline fraction is only 47 volume percent of the total liquid product so that it would have an aromatic content of 2.13% due to the concentration factor alone

$$(1\% \times \frac{100}{47})$$

Thus, the aromatic production was no more than about 2% by weight.

Example 8

This example will illustrate the flexibility which is offered by the novel process of this invention in connection with the subsequent treatments which can be given to the 166°C+ (330°F+) fuel oil products.

A portion of the 166°C+ (330°F+) product (101.5 g) from Examples 4—6 was hydrogenated in a stirring autoclave using Girdler G-49B Ni catalyst (4.1 g), 3549 kPa (500 psig) hydrogen, 177—191°C (350—375°F), over a three hour period repressuring with hydrogen until no further pressure drop. The hydrogenated product had the following properties:

Gravity, °API	48.2
Specific	0.7874

Boiling Range, °C (°F)

10%	165°C	(329°F)
20%	179	(354)
50%	212	(413)
70%	235	(455)
90%	264	(508)
95%	274	(526)
98%	282	(540)

	Pour Point, °C	<-73.3	(<-100°F)
	Freezing Point, °C	<-54	(<-65°F)
5	Aniline No. °C		(179.5°F)
	Aniline-Gravity Product		86,500
10	J/kg ⁽¹⁾	43.8 x 10 ⁶	(18,847 btu/lb)
	Mol. Wt., est.		180
	Hydrogen, wt. %		14.98
15	Carbon, wt. %		85.23
	H/C Ratio		2.09
20	Smoke Point		37
	Luminometer No. ⁽²⁾		>80

⁽¹⁾ Estimated from aniline-gravity product, ASTM D—1405

⁽²⁾ Estimated from smoke point, ASTM D—1740

This material is an excellent premium jet fuel, exceeding JP—7 specifications in freezing point (max. -43°C (-46°F), BTU/lb (Min. 18,700; 43.5 x 10⁶ J/kg) and luminometer No. (Min. 75). The overall properties indicate it is highly isoparaffinic.

Example 9

A mixture of propylene/isobutene/propane/n-butane/isobutane, 35/22/16/6/21 wt.%, was charged to a pilot plant over HZSM-5 extrudate catalyst at 446 kPa (50 psig), 1.2 LHSV (olefin), no gas recycle, reactor inlet temperatures 268°C (514°F), outlet 283°C (541°F) for 2-1/2 days. Propylene conversion of 2—2 1/2 days was 91%, butene 51%, and C₆+ octane No. (R+O) 91.3 C₆+ composition was as follows:

	Paraffins, Total	34	
	Iso		29
40	Normal		5
	Olefins	55	
45	Naphthenes	2	
	Aromatics	9	
		100%	

This liquid product was tested for gum stability by ASTM Test D—873, 5 hours, using an additive package consisting of 6.8 kg (15 lbs) antioxidant (2,6-ditert, butyl p-cresol) and 2.3 kg (5 lbs) metal deactivator (N,N'-disalicylidene-1,2-propane diamine) per 1000 bbl. Potential gum was high, 300 mg/100 ml. A good result is considered to be 10 mg/100 ml.

Examples 10—14

The liquid product from Example 9, composed of 1% propane, 7% C₄'s, 7.5% C₅'s and 84.5% C₆+, was charged over the extruded catalyst of Example 1 containing 65% ZSM-5 at 2859—4928 kPa (400—700 psig), 260—288°C (500—550°F), 0.5—3 LHSV, for 3 days.

The actual operating conditions, as well as the results obtained are shown in the following table:

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TABLE

Example	C	10	11	12	13	14
LHSV	H	0.6	1.1	0.4	0.5	2.0
WHSV		0.9	1.5	0.6	0.7	2.7
Temp., °C, Average	A	263	264	264	290	289
Maximum	R	270	269	271	299	292
Run Time, Hours		18	6 1/2	16	24	2
Accumulative Time, Days	G	0.8	1.0	1.7	2.7	2.8
Pressure, kPa	E	← 2859 →		← 4928 →		
Liquid Product Gravity, °API		56.4	43.7	44.7	45.8	43.2
Yield, Wt. %						43.1
C ₁ +C ₂		<0.1	<0.1	<0.1	0.1	<0.1
C ₃		0.7	1.4	1.3	1.1	2.5
C ₃ =		<0.1	<0.1	<0.1	<0.1	<0.1
i-C ₄		4.1	6.6	6.6	7.0	8.6
n-C ₄		2.1	2.7	2.7	2.9	4.2
C ₄ =		1.1	0.3	0.4	0.3	0.4
i-C ₅		1.8	4.2	4.0	4.7	6.5
n-C ₅		0.8	1.3	1.0	1.3	2.6
C ₅ =		4.9	0.4	0.5	0.5	0.4
C ₆ +		84.5	83.1	83.4	82.2	74.8
		100.0	100.0	100.0	100.0	100.0

TABLE (continued)

Example		10	11	12	13	14
Liquid Product Boiling Range, °C (°F)		70°C (158°F)	61°C (142°F)	64°C (147°F)	56°C (134°F)	78°C (171°F)
10%	45°C (114°F)	128	120	123	118	129
30	98	(261)	(248)	(254)	(243)	(263)
50	131	(319)	(309)	(313)	(312)	(324)
70	155	(377)	(382)	(368)	(401)	(412)
90	191	(469)	(477)	(456)	(530)	(527)
95	206	(496)	(504)	(485)	(570)	—
98	220	(511)	—	(500)	—	—
% Boiling Above 166°C (330°F)	22	43	42	41	44	48
% Boiling Above 193°C (380°F)	9	30	36	28	34	37

From the above table, it can be seen that Examples 10, 11, 12 and 14 all resulted in successful operation as witnessed from the fact that the C_6+ liquid fraction of these examples was no more than 5% by volume less than the liquid fraction of the charge. Example 13, however, was run at a severity which is simply too high. Note that this example obtained a C_6+ liquid yield of 74.8 volume percent which is 11.5 volume percent less than the charge. Also note that in this example, the C_5 total yield was higher than the C_5 total of the charge. The above results with Example 13 indicate that significant cracking took place as opposed to the polymerization of high gum forming olefins.

All of the liquid products from Examples 10—14 were composited and distilled cut point 166°C (330°F). The 45.5 volume percent gasoline product boiling below 166°C (330°F) had the following properties:

	Gravity, °API	63.0
	Specific	0.7275
15	Boiling Range, °C (°F)	
	10%	51°C (124°F)
	20%	62 (144)
20	50%	109 (229)
	70%	135 (275)
25	90%	155 (311)
	95%	162 (323)
	98%	170 (339)
30	Octane No. R+O	~80
	Potential gum, mg/100 ml	3
35	C_6+ Composition, wt. %	
	Paraffins, Total	67
	Iso	59
40	Normal	8
	Olefins	12
	Naphthenes	6
45	Aromatics	15
		100%

50 The 54.5 Vol.% 166°C+ (330°F+) product had the following properties:

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	Gravity, °API	30.7	
	Specific	0.8724	
	Boiling Range, °C (°F)		
5	10%	161°C	(321°F)
	20%	173	(344)
10	50%	205	(401)
	70%	229	(443)
15	90%	252	(485)
	95%	256	(494)
	98%	260	(500)
20	Pour Point, °C	<38	(<100°F)
	Aniline No. °C	34	(93.4°F)
25	Diesel Index		29

It can be seen that gasoline gum, using the same additive package used for the charge (Example 9) was very good, 3 mg/100 ml. Research octane No. was lower, due to the high concentration of paraffins which are not believed to be highly branched.

It is again to be specifically noted that the above results also demonstrate that there is substantially no net increase in aromatics even though the aromatics are concentrated in the gasoline fraction. Thus, for example, the charge material had an aromatic content of 9 weight percent (Example 9). The gasoline fraction had an aromatic content of 15 weight percent. However, the gasoline fraction only represented 45.5 volume percent such that by concentration effects alone

$$(9 \times \frac{100}{45.5})$$

- 5 the aromatics content would have been 19.78 weight percent.

It is also to be specifically noted that the combined liquid product of Examples 10, 11, 12, 13 and 14 meets the aforementioned criteria with respect to the C_6+ liquid yield even though Example 13 does not; thus adding up the C_6+ liquid yield of Examples 10, 11, 12, 13 and 14, it can be seen that it averages to 80.72 volume percent which is less than 5 volume percent below the proportion of the C_6+ liquid fraction of the charge.

Claims

1. A process for enhancing the gum stability of highly olefinic gasoline without producing more than 5 weight percent of aromatics characterized by contacting an olefinic gasoline having an olefin content of at least 50 weight percent with an acidic crystalline aluminosilicate zeolite having a silica to alumina mole ratio of at least 12 and a constraint index of 1 to 12 at a temperature of from 177 to 316°C, a pressure of from 790 kPa to 7000 kPa and a space velocity from 0.2 to 10 LHSV.
2. The process of Claim 1 characterized in that the aromatics produced are less than 5 weight percent.
3. The process of Claims 1 and 2 characterized in that the C_6+ liquid fraction of the product is no more than 5 volume percent less than the C_6+ liquid fraction of said olefinic gasoline charge.
4. The process of any preceding claim characterized in that the crystalline aluminosilicate zeolite used is ZSM-5, ZSM-11, ZSM-12, ZSM-35 or ZSM-38.

Patentansprüche

1. Verfahren zur Verbesserung der Gum-Stabilität von hoch-olefinischem Benzin ohne Erzeugung von mehr als 5 Gew.-% Aromaten, dadurch gekennzeichnet, daß man ein olefinisches Benzin mit einem Olefingehalt von wenigstens 50 Gew.-% mit einem sauren kristallinen Aluminosilicat-Zeolithen mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von wenigstens 12 und einem Zwangsindex von etwa 1 bis 12 bei einer Temperatur von 177 bis 316°C, einem Druck von 790 kPa bis 7000 kPa und einer Raumströmungsgeschwindigkeit von 0,2 bis 10 LHSV in Berührung bringt.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die erzeugten Aromaten weniger als 5 Gew.-% betragen.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die C_6+ -Flüssigfraktion des Produkts nicht mehr als 5 Volumenprozent weniger als die C_6+ -Flüssigfraktion der betreffenden olefinischen Benzincharge ausmacht.
4. Verfahren nach den vorhergehenden Ansprüchen, dadurch gekennzeichnet, daß der verwendete kristalline Aluminosilicat-Zeolith ZSM-5, ZSM-11, ZSM-12, ZSM-35 oder ZSM-38 ist.

Revendications

1. Procédé pour accroître la stabilité de la gomme d'une essence fortement oléfinique sans produire plus de 5% en poids de matières aromatiques, caractérisé par la mise en contact d'une essence oléfinique ayant une teneur en oléfines d'au moins 50% en poids avec une zéolite cristalline acide de type aluminosilicate ayant un rapport molaire de la silice à l'alumine d'au moins 12 et un indice de contrainte d'environ 1 à 12 à une température de 177°C à 316°C, une pression de 790 kPa à 7 000 kPa et une vitesse spatiale liquide horaire de 0,2 à 10.
2. Procédé selon la revendication 1, caractérisé en ce que les matières aromatiques produites constituent moins de 5% en poids.
3. Procédé selon l'une des revendications 1 ou 2, caractérisé en ce que la fraction liquide en C_6+ du produit n'est pas inférieure de plus de 5% en volume à la fraction de liquide en C_6+ de ladite charge d'essence oléfinique.
4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ladite zéolite cristalline de type aluminosilicate utilisée est la ZSM-5, la ZSM-11, la ZSM-12, la ZSM-35 ou la ZSM-38.

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$$(9 \times \frac{100}{45.5})$$

5 the aromatics content would have been 19.78 weight percent.

It is also to be specifically noted that the combined liquid product of Examples 10, 11, 12, 13 and 14 meets the aforementioned criteria with respect to the C_6+ liquid yield even though Example 13 does not; thus adding up the C_6+ liquid yield of Examples 10, 11, 12, 13 and 14, it can be seen that it averages to 80.72 volume percent which is less than 5 volume percent below the proportion of the C_6+ liquid fraction of the charge.

Claims

1. A process for enhancing the gum stability of highly olefinic gasoline without producing more than 5 weight percent of aromatics characterized by contacting an olefinic gasoline having an olefin content of at least 50 weight percent with an acidic crystalline aluminosilicate zeolite having a silica to alumina mole ratio of at least 12 and a constraint index of 1 to 12 at a temperature of from 177 to 316°C, a pressure of from 790 kPa to 7000 kPa and a space velocity from 0.2 to 10 LHSV.

2. The process of Claim 1 characterized in that the aromatics produced are less than 5 weight percent.

3. The process of Claims 1 and 2 characterized in that the C_6+ liquid fraction of the product is no more than 5 volume percent less than the C_6+ liquid fraction of said olefinic gasoline charge.

4. The process of any preceding claim characterized in that the crystalline aluminosilicate zeolite used is ZSM-5, ZSM-11, ZSM-12, ZSM-35 or ZSM-38.

Patentansprüche

1. Verfahren zur Verbesserung der Gum-Stabilität von hoch-olefinischem Benzin ohne Erzeugung von mehr als 5 Gew.-% Aromaten, dadurch gekennzeichnet, daß man ein olefinisches Benzin mit einem Olefingehalt von wenigstens 50 Gew.-% mit einem sauren kristallinen Aluminosilicat-Zeolithen mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von wenigstens 12 und einem Zwangsindex von etwa 1 bis 12 bei einer Temperatur von 177 bis 316°C, einem Druck von 790 kPa bis 7000 kPa und einer Raumströmungsgeschwindigkeit von 0,2 bis 10 LHSV in Berührung bringt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die erzeugten Aromaten weniger als 5 Gew.-% betragen.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die C_6+ -Flüssigfraktion des Produkts nicht mehr als 5 Volumenprozent weniger als die C_6+ -Flüssigfraktion der betreffenden olefinischen Benzincharge ausmacht.

4. Verfahren nach den vorhergehenden Ansprüchen, dadurch gekennzeichnet, daß der verwendete kristalline Aluminosilicat-Zeolith ZSM-5, ZSM-11, ZSM-12, ZSM-35 oder ZSM-38 ist.

Revendications

1. Procédé pour accroître la stabilité de la gomme d'une essence fortement oléfinique sans produire plus de 5% en poids de matières aromatiques, caractérisé par la mise en contact d'une essence oléfinique ayant une teneur en oléfines d'au moins 50% en poids avec une zéolite cristalline acide de type aluminosilicate ayant un rapport molaire de la silice à l'alumine d'au moins 12 et un indice de contrainte d'environ 1 à 12 à une température de 177°C à 316°C, une pression de 790 kPa à 7 000 kPa et une vitesse spatiale liquide horaire de 0,2 à 10.

2. Procédé selon la revendication 1, caractérisé en ce que les matières aromatiques produites constitue moins de 5% en poids.

3. Procédé selon l'une des revendications 1 ou 2, caractérisé en ce que la fraction liquide en C_6+ du produit n'est pas inférieure de plus de 5% en volume à la fraction de liquide en C_6+ de ladite charge d'essence oléfinique.

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ladite zéolite cristalline de type aluminosilicate utilisée est la ZSM-5, la ZSM-11, la ZSM-12, la ZSM-35 ou la ZSM-38.