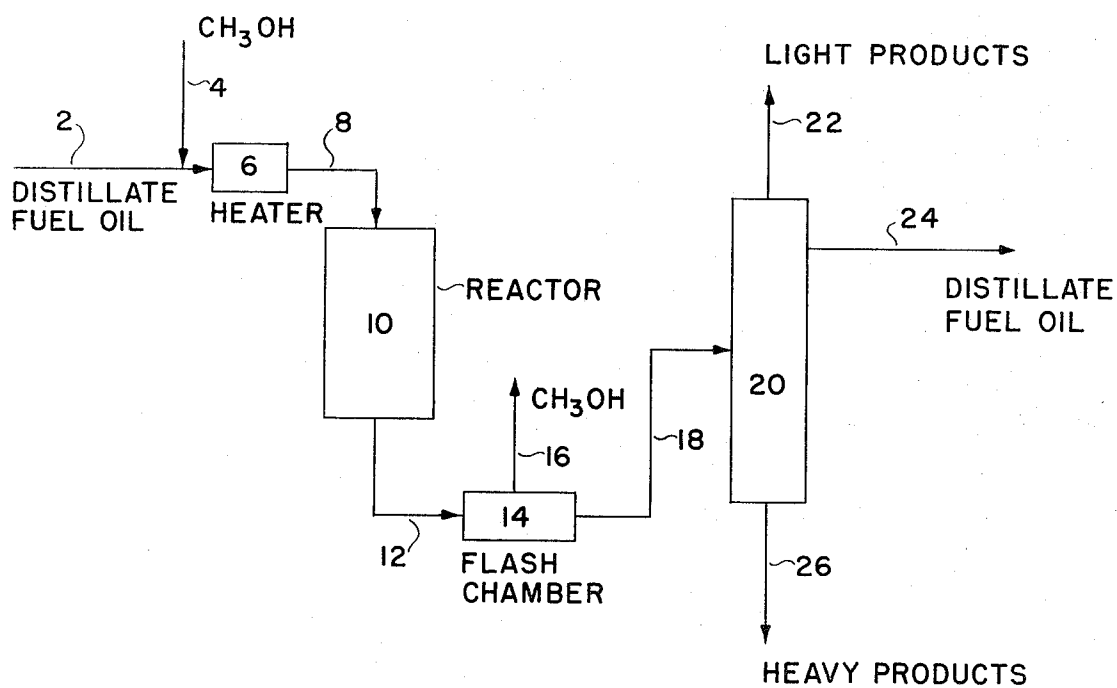


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A SOLID CATALYST AND METHANOL
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ACID NUMBER REDUCTION OF HYDROCARBON FRACTIONS USING A SOLID CATALYST AND METHANOL

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ABSTRACT OF THE DISCLOSURE

The acid number of a hydrocarbon fraction is reduced by contacting the hydrocarbon fraction and a lower alcohol such as methanol with a solid catalyst having a surface area greater than 15 m.²/g., such as alumina or titanium oxide on alumina.

SPECIFICATION

This invention relates to a process for reducing the acid number of hydrocarbon fractions, especially distillate petroleum oils. In particular this invention relates to the use of a solid catalyst in a fixed-bed type process for reducing the acid number of distillate petroleum oils in the presence of compounds like methanol.

It is well known in the petroleum hydrocarbon art that carboxylic acids present in distillate fuels cause considerable problems in the transportation and storage of these oils. For example, the acid number specification of No. 2 fuel oils is less than 0.1. By an "acid number" is meant an acid number determined by ASTM Test No. D974. The fuel oils with higher acid numbers cause unwanted corrosion problems in that the acids attack copper and zinc in the fuel handling systems. In addition, the leached metals then present in the fuel oils tend to reduce the fuel stability and to cause deposit formation on injectors, flow controls and other critical parts of the operating mechanisms.

Previously, the acid number of distillate fuel oils has been reduced by the treatment of these fuel oils with caustic such as sodium hydroxide. This particular method of acid number reduction, however, is fraught with its own problems, namely the formation of foam with the consequent loss of oil and the formation of undesired alkali metal salts such as naphthanates. The alkali naphthanates in turn can decompose to naphthenic acid and caustic upon contact with slightly acidic water. Because of pollution regulations, the naphthenic acids must be disposed of at an undesirably high cost. A mild hydrogenation treatment can also be employed to reduce the acid content of distillate fuel oils, but this process suffers from the high cost of operation. An improved process has now been discovered which tends to overcome many of the difficulties of the prior art processes.

A process has now been discovered which overcomes the disadvantages of the prior art and provides for the reduction of the acid number of a hydrocarbon fraction to a level below 0.1 by ASTM test D974, usually below 0.03 in short contact times of less than one hour, usually less than 30 minutes.

In accordance with the invention, a petroleum fraction having an acid number greater than 0.1 is contacted together with a lower alcohol having the formula: R—OH where R is a lower alkyl group having from 1 to 3 carbon atoms and wherein the amount of said lower alcohol is at least that amount stoichiometrically required to achieve the desired acid number reduction;

at a temperature from 200° F. (93.3° C.) to the thermal cracking temperature of said petroleum fraction;

with a solid catalyst having a surface area greater than 15 m.²/g., said solid catalyst comprising an oxide of a metal selected from the group consisting of the metals from Group IV-B; aluminum; germanium; tin; lead; zinc; and cadmium;

and thereafter recovering a petroleum fraction having an acid number of less than 0.1.

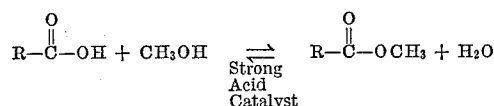
In a preferred embodiment, the hydrocarbon fraction primarily in the liquid phase is passed through a bed of the defined solid catalyst.

CHARGE STOCK

The charge stock for the process of this invention may be any hydrocarbon fraction but in particular a distillate hydrocarbon oil boiling above 330° F., preferably between 330° F. and 650° F. (165.5° C. and 343.3° C.) at atmospheric pressure and having an unacceptably high acid number, as measured by ASTM method D974, typically in excess of 0.1, usually 0.1 to 5. Desirably, the charge stock is a petroleum derived furnace oil or distillate No. 2 fuel oil which boils between 330° F. and 650° F. (165.5° C. and 343.3° C.), although diesel fuels, industrial heating oils, mixtures of the above, and certain acid containing lube oil fractions are also suitable feed stocks for the process of this invention. Hydrocarbon fractions derived from coal, shale or tar sands can also be employed. The fractions are obtained by atmospheric or vacuum distillation techniques or by any other suitable separation procedure from acid containing crude oils; liquid coal fractions; etc.

The distillate fuel oil charge stocks described above are not marketable for reasons given above due to the presence of small amounts of the carboxylic acids such as naphthenic acids. Usually, but not necessarily, the distillate fuel oils also contain small amounts of cresylic acids. The cresylic acid content is not determined by the ASTM method D974. In accordance with this invention, it is proposed to reduce primarily the carboxylic acid content which may be present. While it is not certain, it is theorized that the acids are converted to esters by reaction of the acids with the lower alcohol, e.g. CH₃OH. The best known catalysts for esterification are strong aqueous mineral acids such as sulfuric acid. Unfortunately the reaction is reversible in the presence of water and heat. This reaction is shown in Equation I below:

Equation I



Fortunately a solid catalyst has now been discovered which promotes the irreversible formation of compounds, believed to be esters, from the reaction of the acidic constituents of the distillate fuel oils with, for example, methanol.

REACTANTS

The lower alcohol reactant which is added to the charge stock has the formula: R—OH where R is a lower alkyl group having from one to three carbon atoms per molecule. Examples of suitable alcohols include methanol, ethanol, propanol or isopropanol.

The amount of the lower alcohol to admix with the petroleum charge stock is not critical but should be at least that amount which is stoichiometrically required to reduce the acid number of the charge stock to the desired level. Preferably the reactant is present in an amount equal to at least 10 to 500 times the stoichiometric amount necessary to reduce the acid number to the desired level, more preferably from 10 to 100 times. Since the acid number of the charge is normally low, the amount of the lower alcohol expressed as —OH radical

is usually from 0.3 to 15, more usually from 0.3 to 3, weight percent of the charge stock.

CATALYST

The catalyst for the process of this invention is a solid catalyst having a surface area greater than 15 m.²/g. and comprises an oxide of a metal selected from the group consisting of the metals from group IV-B; aluminum; germanium; tin; lead; zinc; and cadmium. The metals from Group IV-B include titanium, zirconium and haf-

nium. The metal oxide catalyst can be used in an unsupported form so long as the surface area of the metal oxide is at least 15 m.²/g. and is preferably from 50 to 550 m.²/g., more preferably from 100 to 400 m.²/g. The method of preparation of the unsupported metal oxides is not critical so long as the resulting product has the required surface area characteristics. Unsupported metal oxides having lower surface area characteristics than those defined above do not possess sufficient activity to be of interest for the subject reaction. All of the defined metal oxides above have two characteristics in common. First of all, all of the defined metal oxides are members of a class known as n-type semiconductor metal oxides. "N-type semiconductor metal oxides" are defined as semiconductors in which the current is carried predominantly by electrons (see "Solid State Physics," by A. J. Dekker (Prentice-Hall Inc.), Sec. 12-14. Secondly, the above defined metal oxides can exist in a valence state lower than that present in their commonly occurring oxide, i.e. the metal can occur in more than one oxidation state.

The preferred unsupported metal oxides include titanium oxide and aluminum oxide.

While the method of preparation of the unsupported metal oxides is not critical as noted above, the preferred method of preparation of the unsupported titanium oxide is by the hydrolysis of titanium tetrachloride at a pH in excess of 9.

The metal oxides defined above can also be distended or dispersed on any suitable support material well known in the art. Suitable support materials include those supports normally used for this purpose such as alumina, silica or mixtures thereof, thoria or activated carbon. Thus alumina may serve as both a catalyst in its own right and as a support for the other metal oxides.

The supports should have a surface area of between 50 and 1000 m.²/g., usually between 100 and 600 m.²/g. The supports also contain sufficient porosity and mean pore diameter to allow for the entrance and exit of the reactants and products. The usual mean pore diameter of the support is from 30 to 250 Å. The amount of the metal to distend on the support can suitably be from 1 to 50 weight percent of the total catalyst and is preferably from 5 to 25 weight percent of the final catalyst. The metal in the final catalyst is present in the oxide form.

The method of dispersing the metal oxide on the support is not critical, and any methods well known to those having ordinary skill in the art can be employed. For example, the metal can be deposited from an aqueous or organic solution onto the support by the method of minimum excess solution, or the metal can be deposited by vacuum impregnation techniques. The metal is converted to the oxide form by normal calcination techniques.

The attached Figure illustrates one embodiment of the invention. A distillate fuel oil having an unacceptably high acid number generally greater than 0.1 is passed through line 2 and admixed with a desired amount of CH₃OH entering through line 4. The mixture is preheated in heater 6 and passes through line 8 downflow through reactor 10 containing one or more fixed beds of a catalyst consisting of 5 to 25 weight percent titanium on alumina. The charge stock is primarily in the liquid phase. The product having a reduced acid number leaves reactor 10 through line 12 and enters a flash chamber 14 where any excess

CH₃OH is removed overhead through line 16. The liquid products leave chamber 14 through line 18 to distillation zone 20 where light products are recovered overhead through line 22, distillate fuel oil is recovered through line 24 and heavy products are recovered through line 26.

REACTION CONDITIONS

The reaction temperature is suitably from 200° F. (93.3° C.) to the thermal cracking temperature of the charge stock, e.g. usually about 700° F. It is one of the advantages of the process of this invention, however, that the reduction of the acid number can occur under relatively mild conditions. For example, the usual temperatures of reaction are between 200° F. and 490° F. (93.3° C. and 254.4° C.); preferably between 200° F. and 450° F. (93.3° C. and 232.3° C.); and more preferably between 250° F. and 400° F. (121.1° C. and 204.4° C.). The reaction pressure is suitably and preferably close to atmospheric, but higher and lower pressures from 15 to 100 p.s.i.g. can be employed if desired. The liquid hourly space velocity can suitably be from 1 to 20 volumes of charge per volume of catalyst per hour, with preferred space velocities from 1 to 10. v./v./hr. Thus the reaction times are typically from three minutes to one hour, with the usual reaction times being from six minutes to one hour.

The invention will be further described with reference to the following experimental work.

All of the experimental runs were made using a South Louisiana heavy distillate or a Coastal Blend-2 (CB-2-DLM) distillate fuel, the properties of which stocks are given in Table I below.

TABLE I.—INSPECTIONS OF ACIDIC FURNACE OILS

	South Louisiana heavy distillate LR 5998	Heavy distillate fuel (CB-2-DLM) LR 16447
Gravity, D 287, °API.....	35.1.....	34.2.....
Total acid number, D 974.....	0.47.....	0.41.....
Color, D 1500.....	L 1.0.....	0.5.....
Odor.....	Marketable.....	Petroleum.....
Sulfur, D 1266, wt. percent.....	0.10.....	0.09.....
Water, p.p.m.....	24.....	24.....
Carbon residue on 1% bottoms, D 524, wt. percent.....	0.10.....	0.09.....
Aniline point, D 611, ° F.....	162.2- (72.3° C.).....	159.0- (70.6° C.).....
Ash, D 482, wt. percent.....	0.02.....	0.002.....
Stability, 16 hrs. at 210° F.: Existing insolubles, mg./600 g.....	0.7.....	0.5.....
Potential insolubles, mg./600 g.....	1.2.....	0.8.....
Filtrate color, D 1500.....	L 1.0.....	L 0.5.....
Distillation D 86, ° F.: Over point.....	347- (175° C.).....	400- (204° C.).....
End point.....	676- (358° C.).....	644- (340° C.).....
5% by vol. cond. at ° F.....	445- (220° C.).....	445- (220° C.).....
10% by vol. cond. at ° F.....	475- (246° C.).....	483- (253° C.).....
50% by vol. cond. at ° F.....	532- (278° C.).....	542- (283° C.).....
90% by vol. cond. at ° F.....	626- (330° C.).....	604- (318° C.).....
Recovery, percent.....	98.7.....	98.....

Small scale catalyst research runs were made as well as larger scale process runs using the preferred catalysts.

The experimental runs were made in a reactor, externally heated with a tube furnace controlled manually by variacs in the early phases of the project and by ECS temperature controllers in the later stages. The oil and the CH₃OH reactant were fed concurrently and mostly downflow, although the results were not affected by the flow direction. The conditions for the runs using CH₃OH were atmospheric pressure, 5 LHSV, 4 weight percent methanol (about 70 times the stoichiometric requirements), and the desired temperature. In general, the runs were terminated when the product oil exceeded an acid number of 0.1 by ASTM D974 test procedures. This was so, since the acid number specifications for fuel oils is 0.1.

The most widely used support for the catalysts used in the runs below consisted primarily of gamma-alumina. The surface area of this alumina ranges from 150 to 350 m.²/g.; its pore volume from 0.50 to 0.70 cc./g.; and its average pore radius is higher than 40 Å. A detailed tabulation of the properties of two samples of this alumina

appears in Table II. The properties of the preferred catalysts prepared using these aluminas are shown on Table III.

TABLE II.—PROPERTIES OF THE GAMMA-ALUMINA SUPPORTS

Support number.....	SN3-5A17 *	SN3-5A77
BET area, m. ² /g.....	281.9	223.3
Average pore radius, Å.....	44.9	50.3
Pore volume, cc./g.....	0.63	0.56
300-250 Å., percent PV.....	1.2	1.9
250-200 Å., percent PV.....	1.3	4.6
200-150 Å., percent PV.....	2.2	10.6
150-100 Å., percent PV.....	5.1	26.3
100-80 Å., percent PV.....	13.1	12.4
80-60 Å., percent PV.....	25.1	10.5
60-50 Å., percent PV.....	11.8	4.9
50-40 Å., percent PV.....	12.9	4.5
40-30 Å., percent PV.....	12.3	5.3
30-20 Å., percent PV.....	11.8	11.6
20-10 Å., percent PV.....	3.3	7.4
10-0 Å., percent PV.....	0	0

* Greater than 90% gamma alumina.

(3) Solution (2) was impregnated onto the calcined alumina (1) by pouring the solution gradually over the support with continuous mixing of the support.

(4) Immediately thereafter, sufficient distilled water (27 cc.) was added to bring the impregnated alumina to the point of incipient wetness.

(5) The product from (4) was oven dried for 16 hours at 250° F. (121.1° C.) and thereafter calcined at 1000° F. (537.8° C.) for 16 hours.

TABLE IV.—EFFECT OF TI LEVEL ON USEFUL LIFE OF Al_2O_3 SUPPORTED CATALYST

[Atmospheric pressure; 350° F. (176.7° C.); 5 LHSV; 10 cc. of 20 x 40 mesh catalyst; S. La. furnace oil, LR 5998]

Example No.	Ti conc., wt. percent	Catalyst from Table III	Reactant	Throughput of product oil having an acid number of less than 0.1
1.....	6	RN 316-23A	4% MeOH.....	>504
2.....	12	RN 298-25A	4% MeOH.....	1,764
3.....	20	RN 316-24B	4% MeOH.....	2,784
4.....	30	RN 330-15B	4% MeOH.....	1,428

Referring to Table IV, the preferred catalysts are those having 12 to 20% titanium.

TABLE III.—PROPERTIES OF THE MOST PROMISING $\text{Ti}/\text{Al}_2\text{O}_3$ CATALYSTS

Ti level, wt. percent.....	6	12	20
Catalyst number.....	RN 316-23A	RN 298-25A	RN 316-9A
Support number.....	SN 3-5A77	SN 3-5A17	SN 3-5A77
Particle size, unit.....	20 x 40	20 x 40	14 x 30
BET area, m. ² /g.....	191.9	197.8	148.0
Average pore radius, Å.....	51.0	43.8	51.2
Pore vol., cc./g.....	0.49	0.43	0.38
A., percent PV:			
300-250.....	1.1	0.6	1.5
250-200.....	2.1	1.0	2.8
200-150.....	9.8	1.7	11.3
150-100.....	24.6	7.8	23.7
100-80.....	12.4	13.7	11.1
80-60.....	13.3	19.8	11.3
60-50.....	6.7	11.2	5.3
50-40.....	5.7	13.9	6.8
40-30.....	6.7	12.9	8.7
30-20.....	12.7	12.9	13.4
20-10.....	4.9	4.4	4.1
10-0.....	0	0	0

TABLE V.—ACID REDUCTION RUNS WITH $\text{Ti}/\text{Al}_2\text{O}_3$ CATALYSTS

[Atmospheric pressure; 5 LHSV; indicated temperatures; and 4 weight percent methanol in the charge stock (LR 16447)]

Example number	Catalyst	Temperature ° F. ° C.	EOR* acid number	Throughput of oil to indicate acid number (vol./vol.)
5.....	6% Ti (RN 343-3A).....	350 176.7	<0.03	>3,390
6.....	12% Ti (RN 316-9A).....	200 93.3	0.1	11
7.....	12% Ti (RN 316-9A).....	250 121.1	0.1	60
8.....	12% Ti (RN 316-9A).....	300 148.8	0.06	>680
9.....	12% Ti (RN 316-9A).....	350 176.7	0.06	>1,225
10.....	12% Ti (RN 316-9A).....	400 204.4	<0.03	>930
11.....	12% Ti (RN 316-9A).....	490 254.4	<0.03	>1,360

*End of run.

A series of runs were made using the reactor described above and several titanium on gamma-alumina catalysts containing from 6 to 30 weight percent titanium as titania at a temperature of about 350° F. using the furnace oil distillate (LR 5998) whose properties are shown on Table I. These runs were made by passage of the preheated oil plus methanol downflow through a bed of the catalyst. These runs as Examples 1-4 are summarized in Table IV below.

A typical preparation of a catalyst (RN 298-25A) is as follows:

- (1) About 100 cc. of 20x40 mesh alumina (SN 3-5A17), whose properties are given on Table II above, were calcined at 1000° F. (537.8° C.) for 16 hours. The dry weight of the support was 56.18 grams.
- (2) TiCl_4 (33.39 grams) was dissolved in enough n-heptane to form 56 ml. of total solution.

Another series of runs was made as shown in Table V above using the heavy distillate fuel (LR 16447), whose properties appear in Table I.

Referring to Table V, it can be seen that the preferred operating temperature in excess of 250° F., more preferably in excess of 350° F.

Another series of runs similar to those in Table V was made except the catalysts were the aluminas shown in Table II above. The results are summarized in Table VI below.

TABLE VI.—ACID REDUCTION RUNS WITH Ti/Al_2O_3 CATALYSTS

[Atmospheric pressure; 5 LHSV; indicated temperatures; and 4 weight percent methanol in the charge stock (LR 10447)]

Example number	Catalyst	Temperature		EOR* acid number	Throughput of oil to indicate acid number (vol./vcl.)
		° F.	° C.		
12.....	Al_2O_3 (SN3-5A77).....	200	93.3	0.1	47.5
13.....	Al_2O_3 (SN3-5A77).....	250	121.1	0.1	47.5
14.....	Al_2O_3 (SN3-5A77).....	300	148.8	0.05	>550
15.....	Al_2O_3 (SN3-5A77).....	350	176.7	0.08	>1,125
16.....	Al_2O_3 (SN3-5A17).....	425	218.3	0.03	>3,505
17.....	Al_2O_3 (SN3-5A17).....	490	251.4	<0.03	>3,505
18.....	Al_2O_3 (SN3-5A17).....	550	287.8	0.03	>1,365

*End of run.

Referring to Table VI, it can be seen, again, that the preferred operating temperature is in excess of 250° F., more preferably in excess of 350° F.

A further run was made using unsupported TiO_2 prepared by the hydrolysis of $TiCl_4$ at a low pH.

EXAMPLE 19

Example 4 was repeated except unsupported TiO_2 (about 60% titanium) was used as the catalyst. The BET surface area of the TiO_2 was 103 m.²/g. The throughput of oil having an acid number of less than 0.1 was 2780.

Resort may be had to such variations and modifications as fall within the spirit of the invention and the scope of the appended claims:

We claim:

1. A process for treating a hydrocarbon fraction having a carboxylic acid content as measured by an acid number in excess of 0.1 to produce a product having a reduced carboxylic acid content as measured by an acid number of less than 0.1 which comprises:

contacting said petroleum fraction and a lower alcohol having the formula: ROH where R is a lower alkyl group having from 1 to 3 carbon atoms and wherein the amount of said lower alcohol is at least that amount stoichiometrically required to reduce the acid number of the hydrocarbon fraction from in excess of 0.1 to less than 0.1;

at a temperature from 200° F. to the thermal cracking temperature of said petroleum fraction; and

with a solid catalyst having a surface area greater than 15 m.²/g. comprising an oxide of a metal selected from the group consisting of the metals from Group IVB; aluminum; germanium; tin; lead; zinc; and cadmium.

2. A process according to claim 1 wherein the hydrocarbon fraction is a distillate petroleum fraction; the lower alcohol is methanol; and the solid catalyst comprises an oxide of a metal selected from aluminum and titanium and wherein said solid catalyst has a surface area from 50 to 550 m.²/g.

3. A process according to claim 2 wherein the oxide of titanium is deposited on a support.

4. A process according to claim 3 wherein the support is alumina and wherein said contacting occurs at a temperature from 200° F. to 490° F.

5. A process according to claim 4 wherein the catalyst contains from 5 to 25 weight percent titanium.

6. A process according to claim 5 wherein the charge stock is a distillate petroleum fraction boiling between 330° F. and 650° F.

7. A process for reducing the carboxylic acid content of a hydrocarbon fraction which comprises:

passing said hydrocarbon fraction primarily in the liquid phase together with a lower alcohol having the formula: ROH where R is lower alkyl group having from 1 to 3 carbon atoms and wherein the amount of said lower alcohol is from 0.3 to 15 weight percent of said hydrocarbon fraction;

through a bed of a solid catalyst having a surface area greater than 15 m.²/g. comprising an oxide of a

metal selected from the group consisting of the metals from Group IVB; aluminum; germanium; tin; lead; zinc; and cadmium at a temperature from 200° F. to the thermal cracking temperature of said hydrocarbon fraction;

and thereafter recovering a hydrocarbon fraction having a reduced carboxylic acid content.

8. A process according to claim 7 wherein said lower alcohol is methanol; said hydrocarbon fraction is a distillate petroleum fraction; the amount of methanol is from 0.3 to 3 weight percent of the distillate petroleum fraction; said solid catalyst has a surface area from 50 m.²/g. to 550 m.²/g.; and the reaction temperature is from 200° F. to 700° F.

9. A process according to claim 8 wherein the solid catalyst has a surface area from 100 to 400 m.²/g. and the reaction temperature is from 250° F. to 490° F.

10. A process according to claim 9 wherein said catalyst is at least one metal oxide selected from the group consisting of alumina and titania.

11. A process according to claim 10 wherein the catalyst is alumina.

12. A process according to claim 10 wherein the catalyst is unsupported titania.

13. A process according to claim 10 wherein the catalyst is from 5 to 25 weight percent titanium present as the oxide on alumina.

14. A process according to claim 13 wherein the reaction temperature is from 250° F. to 400° F.

15. A process for treating a hydrocarbon fraction having a carboxylic acid content as measured by an acid number in excess of 0.1 to produce a product having a reduced carboxylic acid content as measured by an acid number of less than 0.1 which comprises:

contacting said petroleum fraction and a lower alcohol having the formula: ROH where R is a lower alkyl group having from 1 to 3 carbon atoms and wherein the amount of said lower alcohol is at least 10 to 100 times that amount stoichiometrically required to reduce the acid number of the hydrocarbon fraction from in excess of 0.1 to less than 0.1;

at a temperature from 200° F. to the thermal cracking temperature of said petroleum fraction; and

with a solid catalyst having a surface area greater than 15 m.²/g. comprising an oxide of a metal selected from the group consisting of the metals from Group IVB; aluminum; germanium; tin; lead; zinc; and cadmium.

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