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CATALYTIC CRACKING OF PRETREATED HYDROCARBON OILS

Filed July 29, 1954

Charge Oil.

PRECIPITATION OF DELETERIOUS IMPURITIES WITH ACID

Extracted Oil

REMOVAL OF PRECIPITATES

Precipitates (little if any oil)

Precipitate-Free Oil

Residual Acid

ACID REMOVAL

Aqueous Medium

Water

DRYER

Increased Capacity of Catalytic Cracking Unit

CONVERSION WITH CRACKING CATALYST

BY

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Walter D. Schmidt
Herman S. Seelig

Increased Yield of Motor Fuel, less Coke

Joseph C. Kitashita
ATTORNEY
This invention relates to the catalytic cracking of pre-treated hydrocarbon oil charging stocks and it pertains more particularly to a combination process for pretreating the hydrocarbon oil and then catalytically cracking it to produce increased amounts of more desirable products.

It is known that the charging stocks to catalytic cracking operations can be improved by extracting with selective solvents (U. S. 2,304,289). Such pretreatment enables an increase in the rate of conversion of the treated charging stock to more desirable or higher quality products. It has also been proposed to treat charging stocks containing nitrogen impurities with anhydrous HCl (U. S. 2,352,256). However, in spite of the widespread use of catalytic cracking, the pretreatment of charging stocks has not found commercial acceptance except for the solvent extraction of catalytic cycle oils. An object of this invention is to provide a commercially attractive method and means for the treatment of catalytic cracking charging stocks which is particularly effective on virgin gas oil and upon thermally cracked charging stocks such as coke still gas oil. A further object is to increase the effectiveness of gas oil extraction processes in preparing charging stocks for catalytic cracking operations and to minimize investment and operating costs required for such pretreatment. An ultimate object is to increase the effective capacity of catalytic cracking units and to obtain increased yields of higher quality products and lower yields of undesirable products from a given amount of charging stock at minimum overall expense. Other objects will become apparent in the course of the detailed description of the invention.

In practicing the invention, a catalytic cracking charging stock such as virgin gas oil, coke still gas oil, or mixtures thereof with other charging stocks is treated with a very small amount of a non-oxidizing acid such as sulfuric acid, hydrogen chloride gas or hydrochloric acid, toluene sulfonic acid, trichloroacetic acid, formic acid, sulfurous acid, and preferably sulfuric acid which is strong but not fuming. The amount of acid which is used is ordinarily less than about 0.5 to 1.0% by weight based on said oil, and beneficial results are obtainable with amounts as low as 0.005% by weight. Treatment of the charging stock with the small amount of acid causes certain of the impurities contained in the charging stock to form dark sludgy precipitates which must be removed from the charging stock before it is sent to the catalytic cracking process. These precipitates do not completely settle from the oil and are difficult to remove by conventional means. We have found that these precipitates can be readily removed by the use of selective solvents of the type useful in extracting lubricating oils, gas oils, and the like. The solvent employed is preferably one which will not be affected by the acid. Examples of such solvents include phenol, 1,1,2-trichloro-1-fluoroethane (chloroform), dimethylformamide, dimethyl sulfoxide, alcohol ethers such as methyl cellosolve and methyl carbitol, liquid SO2 and the like. The selective solvent extraction of the charge stock containing precipitates may be conducted under the conditions ordinarily employed in the art, but it is preferred to conduct the extraction so as to produce a minimum quantity of extracted charge stock. The acid may be contacted with the charging stock to form precipitates of the impurities contained therein, and then the charging stock containing the precipitates may be extracted with the selective solvent to form an extract phase containing the precipitates and preferably only a small amount of extracted charging stock and a raffinate phase which contains the treated oil free of precipitates. It is preferred to contact the charging stock with the acid in the presence of the selective solvent since the quality of the charging stock for catalytic cracking is improved to a much greater extent. By the combination of this latter method of treating the charging stock and then catalytically cracking the treated oil, surprisingly improved results are obtained in the catalytic cracking process over those which are obtained when the pretreatment of the charge oil consists of (1) pretreating with the acid and then filtering out the precipitates from the treated oil, (2) solvent extracting with the selective solvent, and (3) pretreating with the acid to form the precipitates and then extracting with the selective solvent.

When operating in accordance with our invention a number of important advantages are obtained: (1) an increased percentage of charging stock may be converted to lower boiling products, (2) an increased percentage of the charging stock may be converted to motor fuel, and (3) the percentage of charging stock converted to coke is decreased significantly when operating at a given level of conversion of the charging oil to lower boil products. These advantages increase the allowable throughput of charging stock to catalytic cracking units and thereby increase their effective capacity by a substantial amount to produce motor fuel. By employing our invention it is possible to reduce the capital investment required for catalytic cracking facilities by a very substantial amount. The regenerator section of such facilities, and in particular the air compressor units, are a very costly portion of the catalytic cracking facilities. Because of the great reduction in coke formation, the increased in conversion of the charging stock to lower boiling products, and the increased percentage of treated charging stock converted to motor fuel, it is possible to design new catalytic cracking facilities to process a given amount of gas oil using regenerator units of about one-half the size that would be required if the gas oil were not pretreated. After allowing for the investment cost of the pretreating facilities, a substantial savings in investment costs can be realized. If other equipment limitations such as the heating capacity, distillation capacity, and the like in present day operating catalytic cracking facilities are not limiting, the use of our invention may enable the throughput to existing reactor units and the gasoline produced to be increased by as much as 100% or more while using the same regeneration facilities. The tremendous savings in operating costs are apparent.

The invention is illustrated by the following examples and data wherein a coke still gas oil (feed A) obtained from the cracking of a mixture of reduced crudes primarily of West Texas origin and a blend of feed B) of 74% of this coke still gas oil and 26% virgin paraffin distillate were pretreated in accord with our invention and then catalytically cracked over a silica-alumina catalyst to produce motor fuel as the desired product.

Samples of the gas oil blend (feed B) were treated according to three different procedures: (1) treatment with sulfuric acid alone, (2) extraction with methyl cellosolve alone and (3) extraction with methyl cellosolve in the presence of sulfuric acid. The gas oil blend (feed
3 B), which is a blend of 74% of the coke still gas oil (feed A) and 26% virgin paraffin distillate, had an initial boiling point of 365°F and a 50% point of 736°F, an API gravity of 29.2, an aniline point of 156.4°F, a refractive index \( n_D^{20} \) of 1.4923, a sulfur content of 1.479% by weight, and a nitrogen content of 0.097% by weight. The experimental procedure which was followed when treating the gas oil blend with sulfuric acid alone consisted of mixing 1200 cc. (1057 grams) of the gas oil with 3.7 grams of \( \text{H}_2\text{SO}_4 \) (98% concentrated) in a separatory funnel at room temperature. The treatment caused a darkening in the color of the oil due to the formation of precipitates of the deleterious impurities contained in the oil. The mixture of oil and precipitates was allowed to stand overnight to settle a portion of the precipitates. The treated oil was decanted and then passed through filter paper to remove additional amounts of precipitates which remained suspended in the oil. The treated oil was then washed twice with about 300 cc. portions of water to remove any traces of \( \text{H}_2\text{SO}_4 \) which may have remained in the oil. The washed oil was then passed through filter paper to dry it. The two remaining samples of stock converted to motor fuel, and percentage of charging stock converted to coke as the ordinate. The percent conversion (to lower boiling products), percent conversion to motor fuel, and the percentage of charge converted to coke vary in approximately a straight line function with reciprocal space velocity when so plotted on log paper, and therefore, a straight line may be drawn between the data points obtained when the two portions of the same samples were catalytically cracked at different space velocities. With the lines drawn it is possible to interpolate to obtain comparisons as to catalytic cracking results on the untreated and treated samples at either the same percentage conversion of charging stock to lower boiling products or at the same reciprocal space velocity.

The data presented in Table I which follows are interpolated data which were obtained in the above-described manner. The catalytic cracking results were interpolated to the same percentage conversion of gas oil to lower boiling products and were also interpolated to the same space velocity (weight of oil/catalyst/hour), based on the gas oil blend (feed B) charged to the catalytic cracking unit. The results are as follows:

### Table 1

| Run No. | Vol. Methanol/ Vol. Oil | WL Percent on Oil | Conversion of Oxygenates (Vol% of Feed) | Reciprocal of Space Velocity (W/dm³/hr) | Motor Fuel % of Feed | Coke, Wt Percent on Feed | Cracking Throughout Attainable
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>48.0</td>
<td>0.230</td>
<td>27.4</td>
<td>3.29</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.25</td>
<td>48.0</td>
<td>0.315</td>
<td>26.4</td>
<td>2.66</td>
<td>1.21</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.22</td>
<td>48.5</td>
<td>0.222</td>
<td>27.2</td>
<td>2.48</td>
<td>1.39</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.25</td>
<td>43.0</td>
<td>0.250</td>
<td>28.5</td>
<td>2.50</td>
<td>1.54</td>
</tr>
</tbody>
</table>

The volume of oil which could be charged to a catalytic cracking unit operating at a fixed percentage conversion and at the same total amount of coke formed on catalyst. Obtained by dividing wt. percent coke formed with untreated feed by wt. percent coke formed with treated feed.

1200 cc. (1057 grams) of the gas oil blend (feed B) were individually treated at room temperature with 300 cc. of methyl cellosolve in one experiment and with 300 cc. of methyl cellosolve containing 3.7 grams of \( \text{H}_2\text{SO}_4 \) (98% concentrated) in the other experiment. In each experiment the mixture of oil and methyl cellosolve with and without \( \text{H}_2\text{SO}_4 \) was shaken in a separatory funnel for about 5 minutes and then allowed to stand until distinct extract and raffinate phases were formed. The extract layers were withdrawn and diluted with cold water to separate solvent from extracted oil. The raffinate layers were washed twice with about 600 cc. portions of cold water to remove remaining amounts of solvent, and the individual treated oils were dried by passage through filter paper.

Each untreated and treated oil sample was divided into two portions and each portion was catalytically cracked in a laboratory scale fixed bed catalytic cracking unit containing ground silica-alumina catalyst and operating at a block temperature of 950°F. The two portions of each sample were catalytically cracked under substantially the same conditions of temperature, catalyst activity, etc. but employing different contact times, i. e. 30 minutes and 60 minutes in order obtain data on the percentage of charging stock converted to lower boiling products, the percentage of charging stock converted to motor fuel, and the percentage of charging stock converted to coke for each sample at the two different space velocities employed. These data for each sample were plotted on log paper, plotting reciprocal space velocity as the abscissa and percentage conversion of charging stock to lower boiling products, percentage of charging stock converted to motor fuel, and percentage of charging stock converted to coke as the ordinate. The percent conversion (to lower boiling products), percent conversion to motor fuel, and the percentage of charge converted to coke vary in approximately a straight line function with reciprocal space velocity when so plotted on log paper, and therefore, a straight line may be drawn between the data points obtained when the two portions of the same samples were catalytically cracked at different space velocities. With the lines drawn it is possible to interpolate to obtain comparisons as to catalytic cracking results on the untreated and treated samples at either the same percentage conversion of charging stock to lower boiling products or at the same reciprocal space velocity.

The data presented in Table I which follows are interpolated data which were obtained in the above-described manner. The catalytic cracking results were interpolated to the same percentage conversion of gas oil to lower boiling products and were also interpolated to the same space velocity (weight of oil/catalyst/hour), based on the gas oil blend (feed B) charged to the catalytic cracking unit. The results are as follows:

### Table 1

**Comparison on Basis of Same Level of Gas Oil Conversion**

| Run No. | WL Percent on Oil | Conversion of Oxygenates (Vol% of Feed) | Reciprocal of Space Velocity (W/dm³/hr) | Motor Fuel % of Feed | Coke, Wt Percent on Feed | Cracking Throughout Attainable
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>48.0</td>
<td>0.230</td>
<td>27.4</td>
<td>3.29</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>48.0</td>
<td>0.315</td>
<td>26.4</td>
<td>2.66</td>
<td>1.21</td>
</tr>
<tr>
<td>3</td>
<td>0.22</td>
<td>48.5</td>
<td>0.222</td>
<td>27.2</td>
<td>2.48</td>
<td>1.39</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>43.0</td>
<td>0.250</td>
<td>28.5</td>
<td>2.50</td>
<td>1.54</td>
</tr>
</tbody>
</table>

The results shown in Table I when compared on the basis of the same level or percentage of gas oil converted to lower boiling products shows the effectiveness of this combination process in reducing the amount of feed converted to coke. It will also be noted that the percentage conversion to lower boiling products was obtained at lower reciprocal space velocities (higher space velocities). This clearly shows that pretreating the charging stock with the acid and selective solvent enables one to obtain the same rate of conversion of the stock charged to the catalytic cracking unit while operating at a higher space velocity and converting a smaller portion of this stock to coke and a greater portion thereof to motor fuel. It is evident from the data that the capacity or throughput to catalytic cracking units can thus be increased to 153% of its previous capacity while decreasing the size of the regeneration facilities required by about one-third. If it is desired to operate at even higher rates of throughput to the catalytic cracking unit, this may be done but the rate of coke formation will increase. The great reduction in investment and operating costs obtainable when practicing this invention is thus readily apparent. It should also be noted from the data that the percentage of motor fuel produced from the oil charged to the catalytic cracking unit is greatest in run No. 4 wherein the charge stock was treated with a selective solvent containing acid. If the production of motor fuel is based upon the charge stock sent to the pretreating operation, the percentage of such charge which is converted to motor fuel is also highest, i. e. 27.1% for run No. 4, contrasted with 25.8% for run No. 3 wherein the oil was treated only with the selective solvent, and contrasted with 26.1%
for run No. 2 wherein the oil was treated only with the acid. Hence, although some oil is extracted during the pretreating process which can be thermally cracked to produce further amounts of motor fuel, the pretreatment in accord with run No. 4 results in about as much motor fuel produced as from untreated feed. The improvement in the quality of the charging stock is especially noticeable by comparing the results obtained from catalytic cracking of the charge stock at the same space velocities. These data show that much higher conversions with greater amounts of motor fuel are produced from the charge stock which has been pretreated with the acid and the selective solvent than were obtained from the untreated charge stock or from charge stock which had been pretreated either with acid or with selective solvent. Comparisons of the percentage of charging stock converted to coke should be made at the same level of charging stock conversion to lower boiling products, since increase in the percentage conversion of the charge stock represents greater severity of cracking and causes more severe coking.

Samples of the coke still gas oil (feed A) were pretreated by extraction with dimethylformamide in the presence and in the absence of added acid. The procedure which was followed in pretreating the coke still gas oil with dimethylformamide alone consisted of contacting 1125 cc. (1011 grams) of the gas oil with 150 cc. of dimethylformamide in a separatory funnel at room temperature. The mixture was shaken for about 5 minutes and then allowed to stand until distinct extract and raffinate phases were formed. The extract phase was withdrawn and the oil was extracted two more times in this same manner with 100 cc. portions of dimethylformamide each time for a total of 350 cc. of dimethylformamide. The extract layers were combined and the oil separated therefrom by adding water to separate solvent from extracted oil. The raffinate layer was washed twice with 500 cc. portions of water to remove remaining amounts of solvent and the oil was then dried by passing it through filter paper. When the coke still gas oil was treated with the acid in the presence of dimethylformamide, the procedure consisted of contacting 1125 cc. (1011 grams) of the coke still gas oil (feed A) at room temperature with a preformed mixture of HCl in dimethylformamide prepared by passing anhydrous HCl into 150 cc. of dimethylformamide until its volume had increased to 160 cc. (approximately 13.1 grams of HCl). The mixture of gas oil, HCl, and dimethylformamide was shaken in a separatory funnel for about 5 minutes and then allowed to stand until distinct extract and raffinate phases were formed. The extract phase containing the blackish precipitates of the impurities contained in the charge gas oil was darker in color than the raffinate phase. The extract layer was separated and the oil was extracted twice more with 100 cc. portions of dimethylformamide. The extract layers were combined and the oil was separated therefrom by the addition of water. The raffinate layer was then water washed until neutral to litmus paper and then dried by passing it through filter paper. Inspections of the coke still gas oil (feed A) having an initial boiling point of 388° F. and a 90% point of 760° F. before and after the treatment hereinafter described are as follows:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Gas Oil Charge</th>
<th>Dimethylformamide Treated</th>
<th>Dimethylformamide + HCl Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>26.9</td>
<td>27.9</td>
<td>28.7</td>
</tr>
<tr>
<td>Grav., Pt.</td>
<td>165.9</td>
<td>164.9</td>
<td>160.5</td>
</tr>
<tr>
<td>Ref. Index, No. 3</td>
<td>1.5001</td>
<td>1.5050</td>
<td>1.6021</td>
</tr>
<tr>
<td>Sulfur, Wt. Percent</td>
<td>2.19</td>
<td>1.99</td>
<td>1.86</td>
</tr>
<tr>
<td>Nitrogen, Wt. Percent</td>
<td>0.088</td>
<td>0.075</td>
<td>0.011</td>
</tr>
<tr>
<td>Micro Dev Anal., V. Percent</td>
<td>53.5</td>
<td>53.5</td>
<td>52.0</td>
</tr>
<tr>
<td>Odor</td>
<td>6.0</td>
<td>7.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Aromatics</td>
<td>45.5</td>
<td>29.5</td>
<td>39.0</td>
</tr>
<tr>
<td>Oil Extracted by Treatment, Vol. Percent</td>
<td>8.9</td>
<td>6.2</td>
<td></td>
</tr>
</tbody>
</table>

It should be noted from the above inspections that whereas the sulfur content of the gas oil charge is reduced by only about 14% when pretreating with dimethylformamide plus HCl, the nitrogen content is reduced by about 89% by this same pretreatment. In addition, this latter treatment removes only 62% of the oil by extraction whereas treatment with dimethylformamide alone under the same conditions removes 8.9% of the oil, indicating a distinct advantage for pretreating with solvent containing acid.

Each untreated and treated oil sample was divided into two portions and each portion was catalytically cracked in a laboratory scale fixed bed catalytic cracking unit containing ground silica-alumina catalyst and operating at a block temperature of 930° F. The two portions of each sample were catalytically cracked under substantially the same conditions of temperature, catalyst activity, etc. but employing different contact times, i.e. 30 minutes and 60 minutes in order to obtain data on the percentage of charging stock converted to lower boiling products, the percentage of charging stock converted to motor fuel, and the percentage of charging stock converted to coke for each sample at the different space velocities employed. The results for each sample were plotted on log paper in the manner previously described and comparisons of the catalytic cracking results employing untreated and treated samples at the same percentage conversion to lower boiling products and at the same reciprocal space velocity were obtained. These interpolated data are presented in Table II which follows:

### Table II

| Run No. | Treatment of Gas Oil | Conversion, Wt. Percent of Feed | Reciprocal Space Velocity (Wt./Wt. Hr.) | Mutter Fuel (Go-500°F), Wt. Percent of Feed | Coke, Wt. Percent of Feed | Cracking Through, 1 Aromatic
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>5.</td>
<td>None</td>
<td>42.5</td>
<td>0.362</td>
<td>24.3</td>
<td>4.28</td>
<td>1.9</td>
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<tr>
<td>6.</td>
<td>Dimethylformamide</td>
<td>42.5</td>
<td>0.318</td>
<td>26.3</td>
<td>3.18</td>
<td>1.9</td>
</tr>
<tr>
<td>7.</td>
<td>Dimethylformamide + HCl</td>
<td>42.5</td>
<td>0.320</td>
<td>27.4</td>
<td>3.24</td>
<td>2.6</td>
</tr>
</tbody>
</table>

**COMPARISON ON BASIS OF SAME SPACE VELOCITY**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Treatment of Gas Oil</th>
<th>Conversion, Wt. Percent of Feed</th>
<th>Reciprocal Space Velocity (Wt./Wt. Hr.)</th>
<th>Mutter Fuel (Go-500°F), Wt. Percent of Feed</th>
<th>Coke, Wt. Percent of Feed</th>
<th>Cracking Through, 1 Aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.</td>
<td>None</td>
<td>33.3</td>
<td>0.245</td>
<td>22.5</td>
<td>3.00</td>
<td>2.6</td>
</tr>
<tr>
<td>6.</td>
<td>Dimethylformamide</td>
<td>35.5</td>
<td>0.244</td>
<td>24.5</td>
<td>3.00</td>
<td>2.6</td>
</tr>
<tr>
<td>7.</td>
<td>Dimethylformamide + HCl</td>
<td>45.0</td>
<td>0.245</td>
<td>26.0</td>
<td>3.00</td>
<td>2.6</td>
</tr>
</tbody>
</table>

1. The volume of oil which could be charged to a catalytic cracking unit operating at a fixed percentage conversion and at the same total amount of coke formed on catalyst, obtained by dividing wt. percent coke formed with untreated feed by wt. percent coke formed with treated feed.
When the catalytic cracking results are compared at the same percentage of gas oil converted to lower boiling products, the data show that the percentage of charging stock decreased with the decrease in the conversion of coke so that approximately twice as much oil can be charged to the catalytic cracking unit when operating at the same level of conversion before the same amount of coke is formed on the catalyst. At this same level of conversion run No. 7 (wherein the charge stock was pretreated with dimethylformamide) indicates that the amount of throughput, i.e., space velocity, to the catalytic cracking unit can be increased to 180% of that rate of throughput employed in processing untreated charge stock. The quality of the charge stock is very greatly improved as evidenced by the results obtained when equal space velocities were employed in the catalytic cracking tests. The percentage conversion to lower boiling products increased from 33.5% for untreated charge to 36.5% for charge which was pretreated with dimethylformamide (run No. 6). The percentage conversion to lower boiling products increased remarkably to 46% in run No. 7, wherein dimethylformamide containing HCl was employed for pretreating the oil. Similar increases in the percentage of conversion to motor fuel of the oil charged to the catalytic cracking unit are shown by the data. When pretreating, the charge stock with a charge containing HCl as in run No. 7, approximately 22% more of the oil charged to the catalytic cracking unit is converted to motor fuel than for the untreated charge stock. Extracting with dimethylformamide alone results in only a 10% increase. Similar results are obtainable when employing much lesser amounts of HCl than were employed in obtaining the above data. Very good results have been obtained when using dimethylsulfoxide as the selective solvent in place of the dimethylformamide used in the above experiments.

The invention is further described in relation to the appended drawing which forms a part of the specification. This drawing shows in schematic form a process flow diagram for performing the processes of this invention.

The charge oil which may be pretreated may be one customarily employed for catalytic cracking. It may boil from just above the naptha boiling range up to about 800° F. The degree of improvement in the quality of the charge oil when it is pretreated in accord with this invention is greater when pretreating petroleum fractions having higher end boiling points, e.g., 700–800° F. The process of this invention is particularly useful in pretreating fractions containing larger amounts of impurities such as nitrogen compounds and the like which tend to deactivate the catalytic catalyst and/or reduce the conversion of the charge oil to desired products and/or increase the conversion of charge oil to undesired products. California and West Texas origin oils are particularly bad in this respect and are greatly improved when pretreated in accord with our invention prior to their catalytic conversion. The charge oil may be a virgin distillate or one obtained from a catalytic or thermal conversion process. Pretreatment is particularly effective upon virgin charge oils and upon oils obtained from thermal conversion processes such as coke still gas oil, but less so on catalytic cycle oil. A preferred charge oil is a coke still gas oil such as contains a high content of nitrogen compounds and other deleterious materials.

The charge oil is admixed with a non-oxidizing acid stock containing HCl (anhydrous or aqueous), HSO₃ (concentrated but not fuming), sulfuric acid, sulfonic acids such as toluene sulfonic acid and alkaline sulfonic acids, amido sulfonic acids, trichloroacetic acid, trifluoroacetic acid, and the like, concentrated HSO₃ being preferred. The amount of the non-oxidizing acid used will depend upon the amount of deleterious impurities contained in the charge oil, but is usually less than about 1% by weight and may be as little as 0.005% by weight. More acid may be employed but no further improvement in the quality of the charge stock is usually noted, and dependent to some extent upon the particular acid the excess amount may have to be removed from the charge oil. The amount of sulfuric acid and acid employed in the pretreatment step, extraction of the treated oil with the selective solvent will remove some of the excess acid, and no special precautions need be taken to remove residual sulfuric acid since this acid may have a beneficial effect upon the cracking catalyst. The amount of acid that may be determined by adding the acid to the oil until no further formation of dark precipitates are noted. The amount of acid to be used may be related to the nitrogen content of the oil. Approximately 0.05 to 0.5 mol of acid per gram atom of nitrogen may be employed. The charge oil and the non-oxidizing acid are agitated at a temperature below about 300° C, preferably at ordinary atmospheric temperatures since better results are obtainable at these temperatures. A preferred method of operating consists of agitating the charge oil, preferably a coke still gas oil, at ordinary atmospheric temperatures with approximately 0.3 mol of HSO₃ (98% concentrated) per gram atom of nitrogen contained in the oil (usually about 1/4% by weight of HSO₃ or thereabout based upon oil). The treated oil is then freed of the dark sludge-like precipitates which may form after introduction of the non-oxidizing acid. These dark sludge-like materials settle very slowly and incompletely. It has been found that the treated oil containing these precipitates may be freed of them by extracting the oil with a selective solvent such as have heretofore been used in the solvent extraction of petroleum distillates such as gas oils, lubricating oils, and the like. The precipitates will be contained in the extract phase and the precipitate-free oil in the raffinate phase. The conditions employed for extracting the precipitate-containing oil with the selective solvent may be those conditions of temperature, time, ratio of solvent to feed oil, and the like which are well known in the prior art for extracting petroleum distillates with a selective solvent. The selective solvent should preferably be one which will not be affected by the presence of the acid so as to react therewith or otherwise be degraded. Examples of suitable selective solvents are liquid SO₂, p-xylene, B-Dichlorodimethyl ether (chlorox), alcohol ethers such as methyl cellosolve and methyl carbitol, dimethylformamide, dimethylsulfoxide, esters of thiosulfonic acid, tetrahydrofurfuryl alcohol, diacetone alcohol, acetoxyl acetone, and the like. We prefer to operate the extraction process so as to obtain a minimum quantity of oil in the extract phase. This quantity can be minimized by employing slightly more than that amount of selective solvent that is necessary to produce separate extract and raffinate phases. The amount of oil extracted will vary with the selective solvent employed and with the nature of the oil charged, but is generally between about 1 to 20% of the oil charge. After removing the selective solvent and the precipitates from the extracted oil, the latter may be employed as a charge stock to a thermal cracking process or may be used as fuel. When employing this technique for extracting precipitates from the treated oil, preferably a coke still gas oil, it is preferred to employ about 20 to 50 volume percent of liquid SO₂ and to conduct extraction at a temperature between about −10 and 25° C, and under sufficient pressure to maintain the SO₂ in the liquid phase.

A preferred form of this invention consists of contacting the acid with the charge oil in the presence of a selective solvent for the charge oil under conditions suitable for the solvent extraction of the charge oil with the selective solvent. When solvent extracting the charge oil in the presence of the acid, the acid is preferably introduced into the extraction zone by previously dissolving it in the solvent and introducing the solvent, although it may also be directly introduced into the extraction zone if desired. The precipitates which are formed are contained in the extract phase and the raffinate phase.
contains the precipitate-free oil. By our combination process of solvent extracting the catalytic cracking charge stock in the presence of the non-oxidizing acid and then catalytically cracking the treated oil, a considerable improvement is obtained in the rate of conversion of charging stock to lower boiling products with increased yields of motor fuel and a decreased conversion of charging stock to coke over that which is obtained by pretreating the charging stock with the acid alone or by solvent extracting the charging stock in the absence of the acid, or by treating the charging stock with the acid followed by solvent extracting the charging stock. This unexpected advantage of solvent extracting the charge oil in the presence of the non-oxidizing acid makes it a much preferred technique in performing the process of our invention. The selective solvents which may be employed and those which have been described previously for the solvent extraction of gas oils, lubricating oils, or the like provided such solvents are not affected by the acid used. The presence of the acid does not affect the operating conditions ordinarily employed in the solvent extraction of such stocks, so that operating conditions employed in the prior art for solvent extracting such stocks with a particular solvent may be used. We prefer to operate the solvent extraction in the presence of the acid so as to remove a minimum quantity of oil into the extract phase. This may be accomplished in the manner previously related. When operating in this preferred manner, a charge oil such as coke still gas oil is solvent extracted preferentially with 20 to 50 volume percent of liquid SO$_2$ containing about 0.3 mol of H$_2$SO$_4$ (98% concentrated) per gram atom of nitrogen contained in the oil (usually about 0.5% by weight of H$_2$SO$_4$, or thereabout, based on the oil) and conducting the extraction at a temperature of about $10$ to $25^\circ$ C. and under sufficient pressure to maintain the SO$_2$ in the liquid phase.

The precipitate-free oil may then be washed with an aqueous medium as water or an alkaline solution to free the oil of residual amounts of acid which may remain therein as well as any solvent which may not have been removed in the separation thereof from the treated oil. An aqueous caustic solution containing about 10% of NaOH is a suitable alkaline aqueous medium. The precipitate-free oil is washed with the aqeous medium until it is substantially neutral. Water which has become occluded within the oil is then removed therefrom in a drying operation such as by passage through rock salt or other desiccating medium. If desired, the steps of washing precipitate-free oil followed by drying of the oil may be eliminated and the precipitate-free oil sent directly to the catalytic conversion process. We prefer, however, to wash the treated precipitate-free oil and then dry it before catalytically converting the treated oil.

Following this series of operations the treated oil is contacted with a cracking catalyst under conditions to effect catalytic cracking. Conventional cracking catalysts of the natural clay type or synthetic silica-alumina, silica-magnesia, silica-alumina-zirconia and the like may be used. The conditions employed in the catalytic cracking of the treated oil may be approximately within the range as would be employed for non-treated charge oil. However, because of the improvement in the quality of the treated oil for catalytic cracking, less severe conditions may be employed if desired or approximately the same conditions may be utilized. When operating at about the same percentage conversion of charge oil to lower boiling products the capacity of a given plant may be greatly increased. The quality of the charge oil after treatment in accord with our invention is so increased that improved yields of desired products such as motor fuel and lower yields of coke are attainable. The conditions customarily employed in catalytic cracking are a catalyst to oil ratio in the range of 2:1 to 20:1 on a weight basis, a cracking temperature of 800 to 1000°F., e. g. 925°F., a weight space velocity in the range of 0.2 to 10 pounds of oil charged per hour per pound of catalyst in the reactor. The cracking system may be of the fluidized catalytic type or the fixed or moving catalyst bed systems.

It is apparent that many wide embodiments of this invention may be made without departing from the spirit and scope thereof and, therefore, it is not to be limited except as indicated in the appended claims.

We claim:

1. A process for the catalytic cracking of gas oils which contain organic nitrogen compounds in amounts deleterious to the catalytic cracking step, which process comprises simultaneously contacting at least one petroleum gas oil boiling below about 800°F. selected from the group consisting of virgin gas oil and thermally cracked gas oil, with (a) a liquid selective solvent selected from the group consisting of sulfur dioxide, phenol, cresol, B,B'-dichlorodithethyl ether, methyl cellosolve, methyl carbital, dimethylformamide, dimethylsulfoxide, thiosulfonic acid esters, tetrahydrofuranyl alcohol, dicyclopentyl alcohol and acetonyl acetone, and (b) an acid selected from the group consisting of hydrochloric, concentrated sulfuric, sulfurous, sulfuric, amido-sulfonic, trichloroacetic, trifluoroacetic and formic, said acid being used in an amount between about 0.005 and 0.5 percent by weight of said gas oil and said solvent being used in an amount slightly in excess of that necessary to produce a separate extract phase, whereby separate extract and raffinate phases are produced, said extract phase comprising precipitates of said organic nitrogen compounds and a major portion of said solvent and said raffinate phase comprising oil of reduced nitrogen content, dissolved and occluded solvent, separating said raffinate phase from said extract phase, recovering gas oil of reduced nitrogen content from said raffinate phase and contacting said recovered gas oil with a solid catalytic cracking catalyst under conditions to effect catalytic cracking thereof.

2. The process of claim 1 wherein said acid is introduced as a mixture in the selective solvent into said contacting step.

3. The process of claim 2 wherein the acid is sulfuric acid.

4. The process of claim 1 wherein the selective solvent is liquid SO$_2$.

5. The process of claim 1 wherein said acid is concentrated sulfuric acid and said solvent is sulfur dioxide.

6. The process of claim 1 wherein said acid is 98% sulfuric acid and said solvent is methyl cellosolve.

7. The process of claim 1 wherein said acid is hydrogen chloride and said solvent is dimethylformamide.

8. The process of claim 1 wherein said acid is used in an amount between about 0.05 and 0.5 gram mole per gram atom of nitrogen contained in said gas oil.

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