

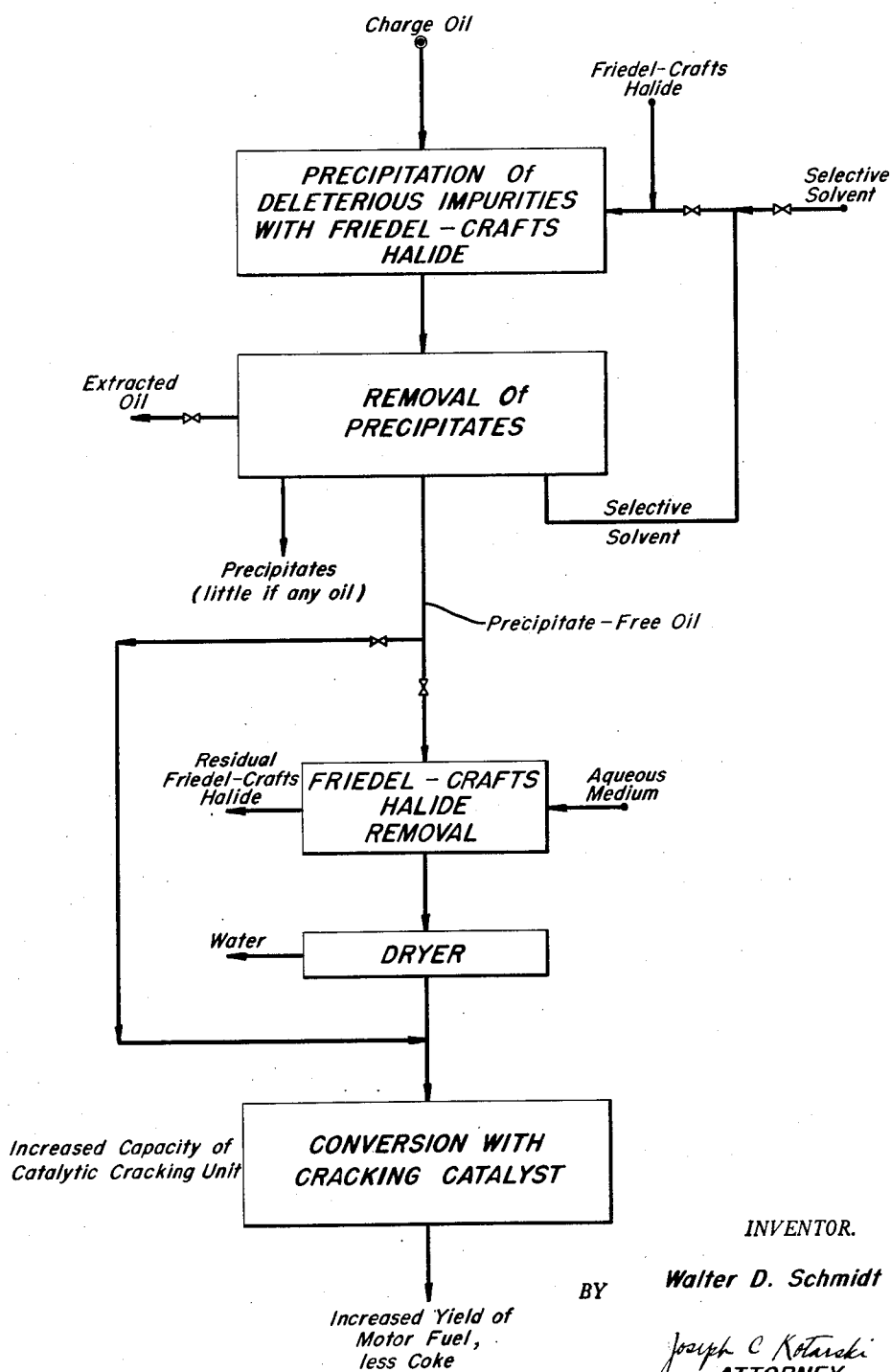
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CATALYTIC CRACKING OF PRETREATED HYDROCARBON OILS

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CATALYTIC CRACKING OF PRETREATED HYDROCARBON OILS

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This invention relates to the catalytic cracking of pretreated 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. 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 Friedel-Crafts halide such as AlCl_3 , BF_3 , FeCl_3 , SnCl_4 , TiCl_3 , and the like. The amount of Friedel-Crafts metal halide 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 Friedel-Crafts halide 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. It has been found that these precipitates can be readily removed by the use of selective solvents preferably of the non-acid polar type useful in extracting lubricating oils, gas oils, and the like. The solvent employed is preferably one which will not be affected by the Friedel-Crafts halide. Examples of these non-acid polar selective solvents are liquid SO_2 and organic polar selective solvents such as phenol, B-B'-dichlorodiethyl ether (Chlorex), dimethylformamide, dimethylsulfolane, meth-

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anol, alcohol ethers such as methyl cellosolve and methyl carbitol, 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 Friedel-Crafts halide 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 Friedel-Crafts halide 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 Friedel-Crafts halide and then filtering out the precipitates from the treated oil, (2) solvent extracting with the selective solvent, or (3) pretreating with the Friedel-Crafts halide to form the precipitates and then extracting with the selective solvent.

When operating in accordance with this 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 sizeably when operating at a given level of conversion of the charging oil to lower boiling 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 this invention it is possible to reduce the capital investment required for catalytic cracking facilities by a 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 increase 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 much smaller size than 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 this invention may enable the throughput to existing reactor units and the gasoline produced to be increased greatly using the same regeneration facilities. The savings in operating costs are apparent.

The invention is illustrated by the following examples and data wherein a coke still gas oil obtained from the coking of a mixture of reduced crudes primarily of West Texas origin was pretreated in accord with this invention and then catalytically cracking over a silica-alumina catalyst to produce motor fuel as the desired product.

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The coke still gas oil employed had the following inspections:

API gravity-----	30.5
Aniline point, ° C-----	72.0
Refractive index, n_D^{20} -----	1.4879
Sulfur, wt. percent-----	0.99
Nitrogen, wt. percent-----	0.091
ASTM distillation:	
IBP=370° F.	
90%=740° F.	

1200 cc. (1048 grams) samples of the above gas oil were extracted with dimethylsulfolane in the absence and in the presence of BF_3 . The experimental procedure which was followed when extracting the gas oil in the absence of BF_3 consisted of contacting 1200 cc. (1048 grams) of the gas oil with 300 cc. of dimethylsulfolane at room temperature in a separatory funnel. The mixture of oil and dimethylsulfolane was shaken for about 5 minutes and then allowed to stand until distinct extract and raffinate phases were formed. The raffinate layer was removed and washed twice with about 600 cc. portions of cold water to remove remaining amounts of solvent, and the treated raffinate oil was then dried by passage through filter paper. When extracting the gas oil with dimethylsulfolane in the presence of BF_3 , the experimental procedure consisted of contact-

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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 sample 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 actually charged to the catalytic cracking unit. The results are as follows:

Table I
COMPARISON ON BASIS OF SAME LEVEL OF GAS OIL CONVERSION

Run No.	Treatment of Gas Oil	Conversion, Wt. Percent of Feed	Reciprocal Space Velocity ($W_o/W_o/\text{Hr.}$)	Motor Fuel ($\text{C}_8-400^\circ\text{F.}$), Wt. Percent of Feed	Coke, Wt. Percent of Feed	Cracking ¹ Throughput Attainable
1-----	None-----	40.0	0.310	26.9	2.47	1.0
2-----	Dimethylsulfolane-----	40.0	0.224	27.4	1.53	1.61
3-----	Dimethylsulfolane+ BF_3 -----	40.0	0.142	28.7	1.17	2.11

COMPARISON ON BASIS OF SAME SPACE VELOCITY

1-----	None-----	36.6	0.270	25.5	-----	-----
2-----	Dimethylsulfolane-----	45.8	0.270	29.2	-----	-----
3-----	Dimethylsulfolane+ BF_3 -----	51.7	0.270	32.9	-----	-----

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.

ing the 1200 cc. (1048 grams) sample of coke still gas oil with a preformed mixture of BF_3 in dimethylsulfolane prepared by passing 4.3 grams of the gaseous BF_3 into 300 cc. of dimethylsulfolane at room temperature. The mixture of oil, dimethylsulfolane, and BF_3 were agitated for about 5 minutes in a separatory funnel at room temperature and then allowed to stand until distinct extract and raffinate phases were formed. It was noted that the extract phase contained blackish precipitates and that the extracted oil was darker in color than the raffinate oil. The extract layer was separated and diluted with cold water to separate solvent from extracted oil and precipitates. The raffinate layer was washed twice with about 600 cc. portions of cold water to remove remaining amounts of dimethylsulfolane and excess BF_3 , and the treated oil was then 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 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 two different space velocities employed. These data for each sample were

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 Friedel-Crafts halide and selective solvents 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. From the above data it can be seen that the rate of throughput or capacity of the catalytic cracking units can be increased substantially while the regeneration facilities required for such increased throughput can be decreased. 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. The data also show that the percentage of motor fuel produced from the oil charged to the catalytic cracking unit is greatest for run No. 3 wherein the charge stock was treated with the selective solvent containing Friedel-Crafts halide. If the production of motor fuel is based upon the charge stock sent to the pretreating operation, calculations show that a higher percentage of the original charging stock is converted to motor fuel when pretreat-

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ing the charge stock with selective solvent containing Friedel-Crafts halide than is produced when pretreating the charging stock with the selective solvent in the absence of Friedel-Crafts halide. The ratio of percentage of charging stock converted to motor fuel divided by the percentage charging stock converted to coke is 10.9 for untreated feed, 17.9 for feed which has been extracted with dimethylsulfolane alone, and 24.5 for the feed which has been extracted with dimethylsulfolane containing BF₃. These results show a decided advantage for the process of this invention in that catalytic cracking of charging stocks pretreated in accord with this invention can be accomplished more selectively to produce increased amounts of gasoline and less coke. The improvement in the quality of the charging stock is especially noticeable by comparing the results obtained from catalytic cracking of the charge stocks 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 selective solvent containing Friedel-Crafts halide than were obtained from the untreated charge stock or from charge stock which had been pretreated with selective solvent in the absence of Friedel-Crafts halide. Comparisons of the percentage of charging stock con-

from extracted oil. The raffinate layer was washed twice with about 600 cc. of hot (150° F.) water to remove any phenol plus unreacted and entrained aluminum chloride from the treated raffinate oil.

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

COMPARISON ON BASIS OF SAME LEVEL OF GAS OIL CONVERSION

Run No.	Treatment of Gas Oil	Conversion, Wt. Percent of Feed	Reciprocal Space Velocity (W _c /W _o /Hr.)	Motor Fuel (C ₅ -400°F.), Wt. Percent of Feed	Coke, Wt. Percent of Feed	Cracking ¹ Throughput Attainable
1-----	None-----	40.0	0.310	26.9	2.47	1.0
4-----	Phenol-----	40.0	0.257	27.2	2.12	1.14
5-----	Phenol+AlCl ₃ ----	40.0	0.187	27.5	1.72	1.41

COMPARISON ON BASIS OF SAME SPACE VELOCITY

1-----	None-----	36.6	0.270	25.5	-----	-----
4-----	Phenol-----	41.3	0.270	27.8	-----	-----
5-----	Phenol+AlCl ₃ ----	47.8	0.270	30.7	-----	-----

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.

verted to coke should be made at the same level of conversion of charging stock to lower boiling products, since an increase in the percentage conversion of the charge stock represents a greater severity of cracking and causes more severe coking.

Samples of the coke still gas oil were pretreated by extraction with phenol in the presence and in the absence of Friedel-Crafts halide. The procedure which was followed in pretreating the coke still gas oil with phenol alone consisted of contacting 1200 cc. (1048 grams) gas oil with 300 cc. of phenol in a separatory funnel at about 230° F. The mixture was shaken for about 5 minutes at this temperature and allowed to settle until distinct extract and raffinate phases had formed. The raffinate phase was removed and washed twice with 600 cc. of hot (150° F.) water to remove phenol. The treated oil from the raffinate phase was then dried by passage through filter paper. The procedure which was followed when contacting the gas oil with phenol in the presence of the Friedel-Crafts halide consisted of contacting 1200 cc. (1048 grams) of the coke still gas oil at 230° F. with a preformed mixture of 300 cc. of phenol containing 10 grams of aluminum chloride. The oil phenol, and aluminum chloride were shaken in a separatory funnel at about 230° F. for about 5 minutes and then allowed to stand until distinct extract and raffinate phases were formed. The extract phase contained the dark color sludge precipitates whereas the raffinate oil was of a lighter color. The extract phase was withdrawn and diluted with hot water to separate phenol

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 converted to coke is lessened by the pretreating steps so that the rate of throughput and the total amount of oil charged to the catalytic cracking unit can be increased greatly when operating at the same level of conversion before the same amount of coke is formed on the catalyst. The selectivity (weight of charge stock converted to motor fuel divided by weight charge stock converted to coke) is distinctly improved over that of the untreated charge stock or charge stock extracted with phenol alone. The quality of the charge stock is greatly improved as evidenced by the results obtained when equal space velocities were employed in the catalytic cracking tests. Run No. 5 shows that an increased conversion of stock charged to the catalytic cracking unit was converted to lower boiling products and likewise an increased percentage of such charging stock was converted to motor fuel. A substantial improvement in these results was obtained by comparison with the cracking results obtained with untreated charge stock or with charge stock which had been extracted with phenol in the absence of aluminum chloride. It was also noted that extraction of the charge stock with phenol in the presence of aluminum chloride resulted in a lower loss of oil to the extract phase than was obtained when extracting the oil with phenol in the absence of aluminum chloride.

Much smaller amounts of Friedel-Crafts halide may

be used in practicing this invention than were employed in obtaining the interpolated data set forth in Tables I and II. Likewise, other Friedel-Crafts halides may be employed although the improvement in the charging stock will not always be the same with various Friedel-Crafts halides.

The invention further described in relation to the annexed 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 naphtha boiling range up to about 800–850° 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. 700–850° F. The process of this invention is particularly useful in pretreating those oils containing large amounts of impurities such as nitrogen compounds and the like which tend to deactivate the conversion 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 this 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 mixed with a Friedel-Crafts halide such as AlCl_3 , BF_3 , BCl_3 , FeCl_3 , AlBr_3 , SnCl_4 , TiCl_4 , SbCl_5 , TeCl_2 , and the like, the use of BF_3 being preferred because a liquid system is more economically operated than one containing solid Friedel-Crafts halides. Gaseous BF_3 is preferred over the aqueous solution of BF_3 . The amount of the Friedel-Crafts halide 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 Friedel-Crafts halide may be employed but no further improvement in the quality of the charge stock is usually noted. If excess amounts of Friedel-Crafts halide are employed in the pretreating step, extraction of the treated oil with the selective solvent will remove some of the excess Friedel-Crafts halide but additional washing of the treated oil with water or alkaline solution may be necessary in order to remove remaining amounts of Friedel-Crafts halide before catalytically cracking the treated oil. The amount of Friedel-Crafts halide required may readily be determined by adding the halide to the oil until no further formation of the dark precipitates is noted. The amount of Friedel-Crafts halide to be used may be related to the nitrogen content of the oil. Approximately 0.05 to 0.5 mol of Friedel-Crafts halide per gram atom of nitrogen may be employed. The pretreating process using these very small amounts of Friedel-Crafts halide is selective in reducing the nitrogen content of the oil and has a lesser effectiveness in reducing the sulfur content. When using BF_3 , a small amount, e. g. 0.1 to 2%, based on oil, of a primary or secondary alkyl fluoride may be separately introduced into the treating zone to enhance the treating effect of the BF_3 . The charge oil and Friedel-Crafts halide are thoroughly agitated at a temperature below about 300° C., preferably at atmospheric temperatures. A preferred embodiment consists of agitating a coke still gas oil at atmospheric temperatures with approximately 0.3 mol of gaseous BF_3 per gram atom of nitrogen contained in the oil (usually about 0.1% by weight of BF_3 or thereabout based upon oil).

The treated oil is then freed of the dark sludge-like

precipitates which were formed after introduction of the Friedel-Crafts halide. 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 of contacting, 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 Friedel-Crafts halide so as to react therewith or otherwise be degraded. The selective solvent should be of the non-acid polar type which includes organic polar selective solvents such as phenol, cresol, B-B'-dichlorodiethyl ether (Chlorex), alcohol ethers such as methyl Cellosolve and methyl Carbitol, dimethylsulfolane, dimethylformamide, tetrahydrofurfuryl alcohol, diacetone alcohol, esters of thiolsulfonic acid, and inorganic polar selective solvents such as liquid SO_2 . It is preferred to operate the extraction process so as to remove 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 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 to produce motor fuel 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 SO_2 and to conduct extraction at a temperature between about -10 and 25° C. and under sufficient pressure to maintain the SO_2 in the liquid phase.

A preferred form of this invention consists of contacting the Friedel-Crafts halide with the charge oil in the presence of a selective solvent for the charge oil and under conditions suitable for the solvent extraction of the charge oil with the particular selective solvent. When solvent extracting the charge oil in the presence of the Friedel-Crafts halide, the Friedel-Crafts halide is preferably introduced into the extraction zone by previously introducing it into the entering selective solvent, although it may be separately 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 this combination process of solvent extracting the catalytic cracking charge stock in the presence of the Friedel-Crafts halide 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 Friedel-Crafts halide alone or by solvent extracting the charging stock in the absence of the Friedel-Crafts halide, or by treating the charging stock with the Friedel-Crafts halide followed by solvent extracting the charging stock. This unexpected advantage of solvent extracting the charge oil in the presence of the Friedel-Crafts halide makes it a much preferred technique in performing the process of this invention. The solvents which may be employed are those non-acid polar selective solvent 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 Friedel-Crafts halide used. The presence of the Friedel-Crafts halide 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. It is preferred to operate the solvent extraction in the presence of the Friedel-Crafts halide 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 preferably with 20 to 50 volume percent of liquid SO_2 containing about 0.3 mol of gaseous BF_3 per gram atom of nitrogen contained in the oil (usually about 0.1% by weight of BF_3 or thereabout based upon the oil) and conducting the extraction at a temperature of about -10 to 25°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 such as water or an alkaline solution to remove residual amounts of Friedel-Crafts halide which may be present therein, particularly when it is employed in excess amounts, as well as any solvent which may not have been removed during its separation 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 aqueous medium until substantially all of the residual Friedel-Crafts halide is removed. It is preferred to dry the washed oil by drying operations such as passage through rock salt or other desiccating mediums prior to catalytically cracking the oil. If the amount of Friedel-Crafts halide is carefully adjusted in the pretreating step so that substantially no residual Friedel-Crafts halide remains in the treated oil after its separation from the selective solvent, the steps of washing with the aqueous medium followed by drying may be eliminated and the precipitate-free oil may be sent directly to the catalytic cracking unit. It is preferred, however, to wash the treated precipitate-free oil and then dry it before it is sent to the catalytic cracking unit.

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. 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 catalyst type or the fixed or moving catalyst bed systems. 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 this invention is so increased that improved yields of desired products such as motor fuel and lower yields of coke are attainable.

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 deleterious in the catalytic cracking step, which process comprises contacting at least one gas oil selected from the group consisting of virgin gas oil and gas oil obtained from the thermal cracking of petroleum simultaneously with a selective solvent and with between about 0.05 and 0.5 gram mol of a Friedel-Crafts halide per gram atom of nitrogen contained in said gas oil and thereby forming precipitates of nitrogen compounds, carrying out the contacting of the gas oil simultaneously with the Friedel-Crafts halide and with an amount of a selective solvent slightly in excess of that necessary to produce separate extract and raffinate phases, thereby forming an extract phase which contains precipitates of the nitrogen compounds together with a minimum amount of the contacted gas oil and a raffinate phase containing the treated gas oil which has substantially the same percentage of aromatic hydrocarbons as the gas oil charged to the contacting step, recovering the treated gas oil from the raffinate phase and contacting the treated gas oil with a solid catalytic cracking catalyst under conditions to effect catalytic cracking thereof.

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

3. The process of claim 1 wherein said Friedel-Crafts halide is BF_3 .

4. The process of claim 1 wherein the selective solvent is liquid SO_2 .

5. The process of claim 1 wherein the treated gas oil is washed with water until substantially neutral prior to contacting the treated gas oil with the cracking catalyst.

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