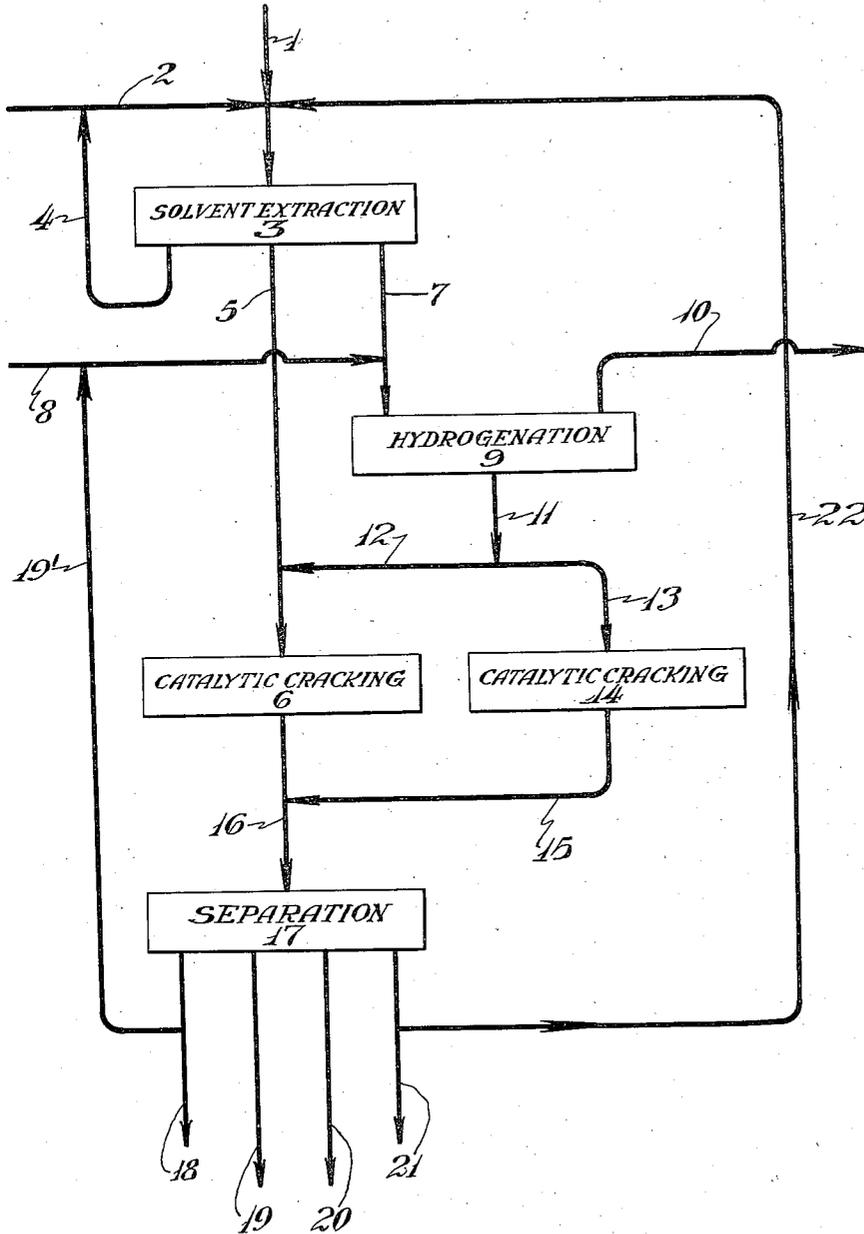


April 14, 1942.

W. L. BENEDICT ET AL
TREATMENT OF CRACKING STOCKS

2,279,550

Filed March 31, 1939



INVENTORS:
Wayne L. Benedict
Jacob Elston Ahlberg
By *Lee J. Garg* Attorney

UNITED STATES PATENT OFFICE

2,279,550

TREATMENT OF CRACKING STOCKS

Wayne L. Benedict and Jacob Elston Ahlberg,
Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application March 31, 1939, Serial No. 265,216

8 Claims. (Cl. 196—13)

The present invention concerns an improved method for the catalytic conversion of hydrocarbon distillates, and more particularly, with the method of treating such distillates prior to their conversion by catalytic methods.

More specifically, the invention deals with the solvent extraction of such distillates by means of immiscible solvents which have a selective action of removing undesirable components of the charging stock and further treatment of the extracted material prior to conversion of such stocks to motor fuel by means of catalytic cracking. While the oils processed are generally from petroleum sources, the scope of this invention is by no means limited to such oils but may include hydrocarbons obtained by the distillation of coal tar, shale oil, etc.

The reactions undergone by hydrocarbons when cracking by non-catalytic methods have been studied and are understood. When using catalysts to assist the thermal conversion of distillates, the reactions are not so well known and as a consequence a discussion involving such reactions is best kept on a factual basis.

The use of treating materials prior to or following non-catalytic cracking has been practiced before, and the primary purpose of such treatment is (a) the production of an improved product, such as, for example, a gasoline having a reduced sulfur content or improved color; (b) for the elimination or reduction of corrosion in cracking equipment such as may be caused by the reaction at high temperatures of hydrogen sulfide with the metallic parts of the cracking plant; or corrosion of condensing equipment and lines by hydrogen chloride formed because of the presence in the crude oil charging stock of hydrolyzable salts; and (c) to reduce coke deposition. The pretreatment of oils does not, however, have the effect of materially increasing the yields of gasoline obtainable from non-catalytic cracking processes.

In one specific embodiment the invention comprises treating hydrocarbon oils with selective solvents to remove therefrom undesirable components, recovering the extracted oil, hydrogenating said extract in contact with a hydrogenation catalyst at hydrogenating conditions, contacting said hydrogenated oil and the raffinate from the extraction step, in vaporious form and in the same or separate stages, with a cracking catalyst at catalytic cracking conditions, separating the gas and gasoline, and returning the unconverted or insufficiently converted oil to the solvent extraction step.

Certain stocks are susceptible to catalytic cracking under moderate conditions, while distillates from other sources are found to be more refractory so that they cannot be cracked to produce adequate yields of gasoline without employing operating conditions which are excessively severe and the benefits of catalytic cracking are materially reduced. Such oils can be improved as charging stocks for the catalytic cracking process by extraction therefrom by well known solvents of the materials which bring about the undesirable effects observed. Among the solvents which may be used for this purpose are liquid sulfur dioxide, furfural, nitrobenzene, phenol, cresol, $\beta\beta$ dichlorethylether, various glycol ethers and many others which have selective solvent effects and which are capable of being recovered from the oil by one of several well known methods. Such methods include precipitation of the solvent by the addition of another material which renders it immiscible with the oil, and by distillation where the oil and the solvent boil in different ranges.

Of the many solvents useful in our process, liquid sulfur dioxide is preferred. The method of carrying out the extraction step is well known and need not be described in detail. The selectivity of the solvent can be varied by the amount of solvent and temperature of the extraction.

It has been found that hydrogenation of the oil prior to catalytic cracking results in considerable improvement in its properties as a charging stock. It is known that the unconverted bottoms from catalytic cracking are not as readily susceptible to conversion as the original crude fraction. These bottoms can be improved so as to reduce the amount of oil recycled during the catalytic cracking step because of increased conversion per pass of the hydrogenated bottoms over the yields obtainable under the same conditions with unhydrogenated bottoms. There is, however, in the unconverted oil a considerable amount of material which is readily converted to gasoline without further treatment.

The present invention deals with a method of separating by a solvent that portion of the unconverted oil remaining after contact with a cracking catalyst, which does not respond readily to catalytic cracking and treating this extract with hydrogen in the presence of a hydrogenation catalyst and at hydrogenating conditions, thereby converting it to a suitable stock for catalytic cracking. The hydrogen is preferably obtained from the gases produced in the cracking step. The catalysts may include any hydrogena-

tion catalyst, but the preferred catalysts are those which are not readily poisoned by sulfur compounds, such as molybdenum oxide and sulfide. In the absence of catalyst poisons the reduced metal catalysts such as nickel, copper, iron, cobalt, etc., may be used.

In many cases the hydrogenated oil is combined with the raffinate from the solvent extraction step and is cracked together with it in the same catalytic conversion stage. However, it has been found advantageous in many cases to catalytically crack the raffinate in one conversion stage at conditions most suitable for its conversion and to crack the hydrogenated extract in a separate conversion stage. The raffinate will, of course, contain a portion of the oil which has passed through the catalytic cracking step at least once, since both the incoming oil and the unconverted oil are extracted in the same step. The two stocks are somewhat different in character, of course, and may require suitable adjustments of cracking conditions in order to obtain the optimum results.

By extracting the combined feed and hydrogenating the extracted oil only, it is possible to reduce the amount of oil to be hydrogenated so that smaller size hydrogenation equipment may be used, and there is a reduction in losses from handling since only that portion of the oil requiring treatment is hydrogenated. The improved properties of the motor fuel resulting from our process is one of the advantages of the invention. Another advantage is that we are enabled to improve the yields of gasoline and polymerizable gaseous olefins which can be obtained by catalytic cracking. Furthermore, the amount of carbon deposition on the cracking catalyst is decreased so that the time of processing as related to regeneration is materially increased. Since the per pass conversion is also increased, the effect is an increase in plant capacity for a given size of equipment.

Our work indicates that treatment of cracking stocks prior to catalytic cracking not only improves the properties of the gasoline but beneficially influences the course of the catalytic reaction. Whereas, in certain instances when cracking untreated oils the catalytic effect is apparently suppressed, treating the same distillate permits the catalytic benefit to be realized.

The motor fuel products of catalytic cracking are, in general, of a marketable quality, requiring only sweetening and the addition of gum inhibitors which are specific for preventing the formation of objectionable gums, color, or other reaction products during the storage period of the gasoline. The products of thermal cracking, on the other hand, often require drastic treatment prior to marketing.

In the case of the catalytic cracking process, the pretreating step is primarily concerned with the production of a suitable charging stock which may be catalytically converted in an economical manner. The reasons for the improvements observed are not known. It may be that there are present in the distillate compounds that tend to inhibit the carbon-carbon cleavage which characterizes catalytic as opposed to non-catalytic cracking. Whatever the explanation, the beneficial effect has been observed in a great many instances, and we do not limit ourselves to any explanation given herein.

Any cracking catalyst which has been found suitable for the conversion of high-boiling hydrocarbons into the gasoline distillate range may be

satisfactorily used in our process. This includes catalysts comprising activated alumina in conjunction with various metal oxides, such as chromia, as well as the various clays and other natural earths which have been treated with acids or other chemical methods, as well as synthetic catalysts prepared from silica and various refractory oxides.

Although the present process may have more or less applicability when using cracking catalysts which may be produced by the chemical treatment of naturally occurring clays, the preferred catalyst comprises specially prepared synthetic masses, for example, silica-alumina, silica-zirconia, silica-alumina-zirconia, and silica-alumina-thoria having a very high degree of activity. These masses are prepared by combining the constituents in various ways, such as mixing, coprecipitation, and the like, under conditions whereby alkali metal ions are excluded. In these catalysts the ratio of the components may vary within wide limits and the masses may be considered to comprise intimate or possible molecular admixtures, all of the components indicating more or less low activity individually, but in the aggregate displaying high activity. The activity also is not an additive function of the individual component, it being relatively constant for a wide range of proportions whether in molecular or fractions of molecular proportions. It appears that no one component can be determined as the one component for which the remaining components may be considered as the promoter according to conventional terminology. In the present invention, these catalysts are used in the form of sized particles or other formed shapes such as pellets produced by compression or extrusion methods. The pressed composites, after drying and forming into definite shapes, are calcined at temperatures above 800° F. prior to contacting with the hydrocarbons.

The cracking step is carried out at a temperature within the range of approximately 800°-1200° F. and only sufficient pressure to insure passage of the oil vapors through the process.

The accompanying drawing illustrates the process diagrammatically. In the drawing, charging oil from line 1 and solvent from line 2 are introduced to solvent extraction zone 3 from which separated solvent is returned to line 2 through line 4. The raffinate passes through line 5 to catalytic cracking zone 6 while the extract is withdrawn through line 7, commingled with hydrogen-containing gas from line 8, and the mixture introduced to hydrogenation zone 9. Gases are withdrawn from zone 9 through line 10 and the hydrogenated extract through line 11. The latter is supplied through line 12 to zone 6 for treatment in admixture with the raffinate or through line 13 to the independent catalytic cracking zone 14. In the latter event, the cracked products from zone 14 are passed through line 15 to commingle in line 16 with the cracked products from zone 6. The cracked products are introduced to separating zone 17 wherein they are separated into a hydrogen-containing gas withdrawn through line 18, a heavier gaseous product containing polymerizable olefins which is withdrawn through line 19, gasoline distillate withdrawn through line 20, and insufficiently converted oil withdrawn through line 21. Hydrogen-containing gas from line 18 may be supplied through line 19' to line 8 and thence to zone 9 for use in the hydrogenation of the extract from zone 3. Insufficiently converted oil from line 21

may be recycled through line 22 to the solvent extraction zone 3.

The following example is given to illustrate the usefulness of our process and is not intended to limit it to the exact conditions given therein.

A California gas oil of 32.3° A. P. I. gravity was extracted with equal parts by volume of liquid sulfur dioxide. The sulfur dioxide was removed from the extract and raffinate by distillation and recovered for further use. The extract was passed to a hydrogenation step, wherein it was hydrogenated in the presence of a molybdenum sulfide catalyst and the hydrogenated oil was passed together with the raffinate into contact with a silica-alumina cracking catalyst at a temperature of 932° F. and a liquid space velocity of four. The gasoline and gas were separated, the unconverted bottoms were returned to the solvent extraction step wherein, together with the incoming crude fraction, they were extracted as previously described and the extract passed into the hydrogenation step and the hydrogenated mixture catalytically cracked. In this manner a total yield of 86% of 81 octane number gasoline was obtained as compared with 78% of gasoline when the combined solvent extraction and hydrogenation steps were omitted. These yields included the gasoline obtained by polymerizing the gaseous olefins produced in the process. The hydrogen for the hydrogenation step was obtained from the gases produced in the catalytic cracking step. The low-boiling gaseous hydrocarbons, methane, ethane, and ethylene were also present since no attempt was made to separate the hydrogen in pure form. There was a reduction in carbon deposition on the cracking catalyst amounting to approximately 50%, so that the ratio of the time for regeneration compared with the time of processing was reduced considerably. This, together with the fact that the per pass conversion was improved, resulted in a material increase in the capacity of the plant.

We claim as our invention:

1. A process which comprises extracting hydrocarbon oil in the presence of a selective solvent, recovering the extracted oil, subjecting said extracted oil to the action of hydrogen in the presence of a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation, contacting the vapor of the hydrogenated extract and the raffinate from the extraction step with a cracking catalyst under conditions adequate to effect substantial catalytic cracking thereof, separating the gas and gasoline, and returning the unconverted oil to the solvent extraction step.

2. The process of claim 1 wherein the solvent comprises essentially liquid sulfur dioxide.

3. A process which comprises extracting hydrocarbon oil with a selective solvent, recovering the extracted oil, subjecting said extracted oil to the action of hydrogen in the presence of a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation, contacting the hydrogenated extract and the raffinate from the extraction step in vaporous form with a composite consisting essentially of a major part of

an especially prepared silica and a minor part of a component selected from the group consisting of alumina and zirconia and substantially free of alkali metal compounds, under conditions adequate to effect substantial catalytic cracking thereof, separating the gasoline, and returning the unconverted oil to the extraction step.

4. The process of claim 1 wherein a portion of the hydrogen-containing gas from the cracking step is used in the hydrogenation step.

5. A process comprising extracting hydrocarbon oil with a selective solvent, recovering the extracted oil, subjecting said extract to the action of hydrogen in the presence of a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation, contacting the raffinate from the extraction step in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking, separately contacting the hydrogenated extract in vaporous form with a separate body of cracking catalyst under conditions adequate to effect substantial catalytic cracking thereof, recovering the gas and gasoline, and returning the unconverted oil from both of said cracking steps to the solvent extraction step.

6. A process comprising extracting hydrocarbon oil with a selective solvent, recovering the extracted oil, subjecting said extract to the action of hydrogen in the presence of a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation, contacting the raffinate from the extraction step in vaporous form with a cracking catalyst comprising essentially a composite consisting of a major part of specially prepared silica and a minor part of a component selected from the group consisting of alumina and zirconia and substantially free of alkali metal compounds, under conditions adequate to effect substantial catalytic cracking, separately contacting the hydrogenated extract in vaporous form with a separate body of cracking catalyst under conditions adequate to effect substantial catalytic cracking, recovering the gas and gasoline, and returning the unconverted oil from both of said cracking steps to the solvent extraction step.

7. In the conversion of hydrocarbons wherein hydrocarbon oil is catalytically cracked and insufficiently converted products separated from gasoline and gas, the method which comprises extracting said products with a selective solvent, hydrogenating the resultant extract, and returning the hydrogenated extract to the catalytic cracking operation.

8. A hydrocarbon oil conversion process which comprises extracting the charging oil with a selective solvent, separating the resultant extract and raffinate, hydrogenating the extract, catalytically cracking the hydrogenated extract and said raffinate, separating the cracked gasoline and gas from insufficiently converted products, and recycling at least a portion of said products to the solvent extraction step.

WAYNE L. BENEDICT.
JACOB ELSTON AHLBERG.