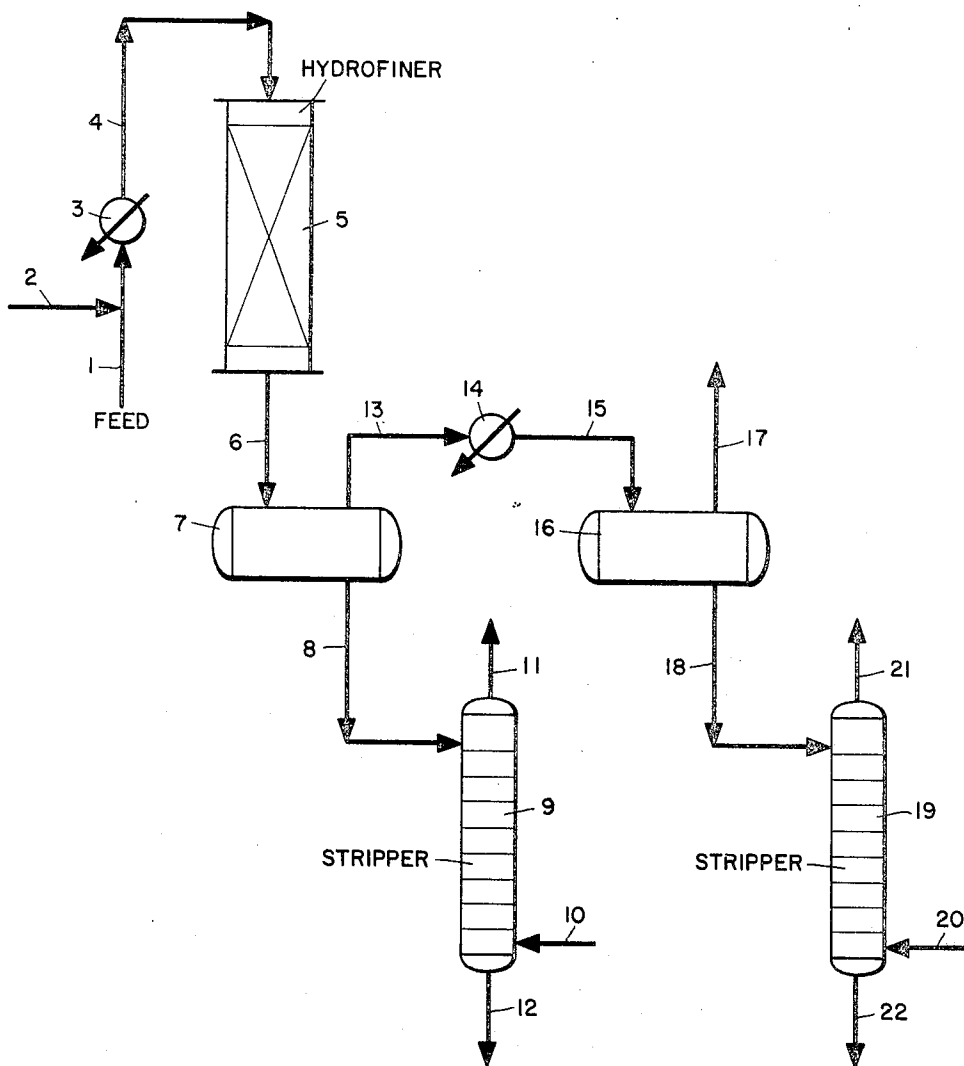


Dec. 9, 1969

J. L. EHRLER

3,483,119

HYDROFINING PROCESSING TECHNIQUE FOR IMPROVING THE  
COLOR PROPERTIES OF MIDDLE DISTILLATES  
Filed March 2, 1966



JOHN L. EHRLER Inventor

By *John J. Schlager*  
Attorney

1

2

3,483,119

## HYDROFINING PROCESSING TECHNIQUE FOR IMPROVING THE COLOR PROPERTIES OF MIDDLE DISTILLATES

John L. Ehrler, Cedar Knolls, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Filed Mar. 2, 1966, Ser. No. 531,161

Int. Cl. C10g 31/14, 23/00

U.S. Cl. 208—264

6 Claims

### ABSTRACT OF THE DISCLOSURE

A middle distillate feed is hydrofined in mixed-phase or vapor-phase operation and the effluent from the hydrofiner is separated into a vapor phase and a liquid phase and the vapor phase is then cooled to condense a liquid hydrocarbon. Each of these liquid fractions is then steam-stripped separately to obtain a light fraction having excellent color properties and a heavier fraction of lesser color improvement. By separating the lighter fraction and stripping it separately to remove light components, there is obtained a light fraction which will meet stringent color specifications.

This invention relates to the catalytic hydrofining of hydrocarbon oils. More particularly, it relates to the catalytic hydrofining of middle distillates wherein a portion of the hydrofined effluent is obtained in the liquid phase, and another portion is obtained in the vapor phase. Still more particularly, the invention is concerned with an improved hydrofining processing technique for the improvement of the color properties of hydrocarbon feeds or portions thereof which is accomplished by vapor-phase or mixed-phase hydrofining, segregation of the hydrofined effluent into a liquid phase and a vapor phase, and separate stripping of fractions contained in each phase.

Various processes are known for removal of sulfur from petroleum distillates including well-known hydrofining techniques wherein the hydrocarbon feed is passed in admixture with hydrogen over a sulfur-resistant hydrogenation catalyst at elevated temperature and pressure such that the sulfur is converted into hydrogen sulfide, which is easily removable from the treated distillate. The present invention is particularly concerned with the hydrofining of middle distillate fractions and is designed to result in improved color properties of the treated fractions, as well as reduced sulfur content. As is well known, the petroleum industry is constantly striving to improve the color stability and initial color properties of various hydrocarbon fractions. Among the numerous methods utilized for achieving good color properties include the aforementioned hydrofining techniques. With conventional hydrofining catalysts, such as, for example, cobalt molybdate on alumina, supported platinum, etc., considerable improvement as regards color is obtained. Hydrofining middle distillates, for example, results in both desulfurization and improved color, depending upon the conditions of temperature, pressure, space velocity, etc. Generally, however, if the color specification is relatively high, e.g., 18 Saybolt, and initial feed color is poor (e.g., 18 Tag Robinson), high pressures in the range of 600 to 1000 p.s.i.g. are required. Alternatively, color improvement can sometimes be accomplished if the hydrofining operation is conducted solely in the vapor phase. It will be appreciated, however, that both these alternatives are considerably more expensive than conventional middle distillate hydrofining techniques. One further alternate would be the rerunning of hydrofined

product which involves redistillation of the hydrofined product and separating therefrom a major proportion of light fractions, leaving a minor proportion of heavy fractions which contain a disproportionate amount of color bodies. As will be appreciated, this alternate is also extremely expensive and often requires the reprocessing of up to 95% of the hydrofined product.

The present invention provides means for overcoming the above disadvantages and obtaining good color properties in those fractions where color specifications must be met. In brief compass, the invention involves (1) subjecting the middle distillate feed to mixed-phase or vapor-phase hydrofining in a catalytic hydrofining zone; (2) separating the hydrofined effluent into heavy liquid and light vapor phases; (3) transferring the heavy liquid phase to a stripping tower wherein the heavy fractions are stripped to remove small amounts of light components and treat gas; (4) cooling the light vapor phase separated from the hydrofined effluent to condense the hydrocarbons contained therein, and to thus form a light liquid phase; (5) separating the condensed light liquid phase from treat gas and gaseous hydrogen-containing products; and (6) transferring the condensed light liquid phase to a second stripping tower wherein it is stripped to remove small amounts of light components. Preferably, step (2) is performed at the temperature and pressure conditions prevailing in the hydrofiner as in the case of mixed-phase operation. Where this is not feasible and/or vapor-phase operation is desired, an intermediate cooling step between (1) and (2) may be required to partially condense the hydrofined effluent.

In this manner the middle distillate feed is hydrofined in mixed-phase or vapor-phase operation and separated into a light fraction and a heavy fraction, which fractions are segregated during subsequent treatment. Both fractions are ultimately stripped separately, thereby resulting in a light fraction having excellent color properties and a heavier fraction having poorer color properties. The heavier fraction is subsequently used for blends having low color specifications, such as diesel oils, while the lighter fraction is used for blends requiring good color properties, such as kerosene.

The invention thus takes advantage of the fact that generally only a portion of the hydrofined effluent must meet stringent color specifications, while the remainder of the product need only meet lenient color specifications with the main requirement usually being one of low sulfur content. Since the hydrofining reactor can either be readily operated in mixed phase so that the effluent exists partly as a vapor and partly as a liquid, or can be operated in vapor phase with the effluent subsequently being partially condensed, the invention takes advantage of the relative ease of separation of the light and heavy phases either at the conditions prevailing in the hydrofiner or subsequent to cooling of the effluent. The good color light fractions existing in the vapor phase (issuing from the hydrofiner or cooler) are immediately segregated and treated separately from the poor color heavy liquid fractions. This procedure is to be distinguished from conventional hydrofining of middle distillates wherein the heavy and light fractions are not segregated but, after intermediate high and low pressure separations, usually are combined as a liquid and stripped together to remove very light components. By segregation of the heavy and light fractions of the middle distillate hydrofined effluent in the present invention, there is obtained a light fraction which will meet stringent color specifications and a heavy fraction having poor color properties, which heavy fraction can be utilized for blends wherein color is no problem. In effect, the present invention takes advantage of the fact that vapor-phase hydrofining will yield

better color products than liquid-phase hydrofining, since in the present invention the light fractions (which are segregated from the poor color heavy fractions in treatment subsequent to the hydrofiner) have actually been treated in the vapor phase. It will be readily appreciated that the present invention offers substantial economic saving over other techniques available for producing good color product such as those previously mentioned, e.g. total vapor-phase treatment, high pressures, and rerunning.

The hydrofining conditions to be employed in the present invention are generally moderate and include a temperature of about 450 to 700° F., preferably 500 to 600° F.; a pressure of about 125 to 500 p.s.i.g., preferably 150 to 250 p.s.i.g.; and a space velocity of about 1.0 to 6.0 v./v./hour, preferably 2.0 to 4.0 v./v./hour. Hydrogen is preferably introduced concurrently with the feed at a rate of about 20 to 5000, preferably 150 to 3000, standard cubic feet of hydrogen per barrel of feed. As mentioned, the operating conditions within the hydrofiner are preferably adjustable so that the operation is conducted in a mixed vapor-liquid phase. More preferably, the particular hydrofining conditions chosen will be sufficient to maintain in the vapor phase that portion of the feed in which the greatest degree of color improvement is desired.

The feedstocks herein contemplated are generally known as middle distillates or distillate fuels, and generally boil in the range of about 300 to 700° F., with the heating oils and kerosenes boiling in the range of about 300 to 500° F., and the diesel fuels boiling in the range of about 500 to 700° F. Higher boiling feeds cannot be economically used in the invention owing to the difficulty and expense of the vaporization.

The hydrofining catalysts employed herein are of the conventional variety. Without being limited to any particular catalyst, these catalysts will typically comprise an alumina or silica-alumina support carrying one or more iron group metals and one or more metals of Group VI-B of the Periodic Table in the form of the oxides or sulfides. In particular, combination of one or more Group VI-B metal oxides or sulfides with one or more Group VIII metal oxides or sulfides are preferred. For example, typical catalyst metal combinations contemplated are oxides and/or sulfides of cobalt-molybdenum, nickel-tungsten, nickel-molybdenum-tungsten, cobalt-nickel-molybdenum, nickel-molybdenum, etc. As a typical example, one catalyst will comprise a high metal-content sulfided cobalt-molybdenum-alumina catalyst containing about 1 to 10 wt. percent cobalt oxide and about 5 to 40 wt. percent molybdenum oxide, especially about 2 to 5 wt. percent cobalt and about 10 to 30 wt. percent molybdenum. It will be understood that other oxides and sulfides will be useful, such as those of iron, nickel, chromium, tungsten, etc. The preparation of these catalysts is now well known in the art. The active metals can be added to the relatively inert carrier by impregnation from aqueous solutions followed by drying and calcining to activate the composition. Suitable carriers include, for example, activated alumina, activated alumina-silica, zirconia, titania, etc., and mixtures thereof. Activated clays, such as bauxite, bentonite and montmorillonite, may also be employed.

Operation of the process of the invention may be more readily understood by reference to the accompanying drawing. The attached figure is a schematic flow diagram illustrating the process of the invention. For purposes of simplicity, only the equipment items needed to comprehend the present process have been shown, with such features as auxiliary piping, pressure control valves, etc. being eliminated.

In the figure a middle distillate feed is introduced to the process through line 1. Hydrogen-rich gas is added to the feed through line 2, and the combined streams are heated in heater 3 and passed through line 4 into hydrofining reactor 5. The oil and hydrogen are preferably supplied

at an elevated temperature and pressure close to that employed in the hydrofiner. Hydrofiner 5 contains a sulf-activated hydrofining catalyst of the type hereinbefore described, preferably in the form of a fixed bed. The operating conditions and hydrofiner 5 are preferably adjusted so that the oil feed exists as a mixed vapor-liquid phase. However, total vapor phase is also contemplated as hereinbefore mentioned. With the preferred hydrofining conditions hereinbefore set forth and with a middle distillate feed boiling in the range of 300 to 700° F., approximately 60 volume percent of the feed will exist as a vapor in the hydrofining reactor, these fractions having a boiling range of about 300 to 550° F. and representing that portion of the feed in which color improvement is most desired.

The hydrofined effluent from hydrofiner 5 passes through line 6 to separator 7 which preferably operates at the hydrofiner temperature and pressure in the case of mixed-phase hydrofining and separates the hydrofined effluent into the vapor and liquid phases essentially existing within the hydrofiner without further vaporization or condensation. (If mixed-phase operation is not feasible and total vapor phase is indicated, a cooler will be required in line 6 to partially condense the hydrofined effluent and to form a heavy liquid phase and a light vapor phase in which color improvement is desired.) The liquid phase comprises partially purified high-boiling fractions which contain but a small amount of dissolved light hydrocarbons and impurities. The vapor phase comprises light hydrocarbons having the aforementioned boiling range, as well as hydrogen, hydrogen sulfide, etc. The liquid phase separated in separator 7 flows by gravity or pressure differential through line 8 to stripper 9. Stripper 9 operates at substantially the pressure existing in hydrofiner 5. Steam is preferably introduced into stripper 9 through line 10 to remove small amounts of light components, such as methane and ethane, as well as hydrogen sulfide, hydrogen, etc. Purified heavy fractions boiling, for example, in the range of 560 to 700° F. are recovered from stripper 9 through line 12. These heavy fractions will have relatively poor color properties and are subsequently used for blends having relatively low color specifications, such as diesel oil blends.

The vapor phase from separator 7, still at substantially the temperature and pressure of hydrofiner 5 (in the case of mixed-phase operation), is withdrawn through line 13 and then cooled in cooler 14, to condense a major portion of the light hydrocarbons contained therein. Preferably, the temperature is reduced to below about 200° F., more preferably about 100 to 175° F. The condensed light hydrocarbons and noncondensable vapors then continue through line 15 to separator 16, wherein the condensed light hydrocarbons separate as a liquid phase from the uncondensed vapors while still at substantially the pressure of hydrofiner 5. Thus, separator 16 most preferably operates at a temperature of about 100 to 175° F. and a pressure of 150 to 250 p.s.i.g., with the preferred middle distillate feed and the preferred hydrofining conditions previously set forth. The vapor phase from separator 16 containing hydrogen, methane and other very light hydrocarbons is removed through line 17; and the liquid phase consisting of the condensed light hydrocarbons, as well as dissolved hydrogen sulfide, hydrogen, etc., are then passed through line 18 to stripper 19, which operates at substantially the pressure existing in hydrofiner 5. Steam is preferably introduced into stripper 19 through line 20 to thereby strip out the gaseous light components, hydrogen sulfide, hydrogen, etc., which are removed through line 21. The purified light hydrocarbon fractions having excellent color properties are removed through line 22 and subsequently used for blends having high color specifications, such as kerosene.

By operating in accordance with the present invention, the middle distillate feed previously described is separated into a heavy fraction having poor color properties and

a light fraction having excellent color properties. The light fractions, for example, have a color hold which is generally at least 5 Tag Robinson color units higher than the feed and generally is better than can be measured on the Tag Robinson color scale. As a specific example, hydrofining a middle distillate feed having a boiling range of about 300 to 700° F. and a color rating of 10 Tag Robinson produced a light fraction having a boiling range of about 300 to 500° F. and a color rating of 20 Saybolt, and a heavy fraction having a boiling range of about 500 to 700° F. and a color rating of 20 Tag Robinson.

The invention is subject, of course, to various modifications. As mentioned, cooling capacity can be added between the hydrofining reactor and the hot separator where vapor-phase operation is desired or to establish greater control over the relative amounts of light and heavy fractions. For example, at the optimum hydrofining temperature, the proportions of light and heavy cuts may not be sufficient to meet product demand. This may be circumvented by cooling the reactor effluent to partially condense a portion of the heavy material.

The scope of the invention should not be construed as limited to the details described above. The true scope of the invention is intended to be embraced by the following claims.

What is claimed is:

1. An improved process for hydrofining a middle distillate feed to enhance the color properties thereof which comprises:

- (1) hydrofining said feed at elevated temperature and pressure in the presence of hydrogen and a hydrofining catalyst wherein the hydrofining conditions are selected to maintain at least a portion of said feed in the vapor phase;
- (2) separating the hydrofined effluent from step (1) into a liquid phase and a vapor phase;
- (3) stripping said liquid phase separated in step (2) with steam to remove dissolved low-boiling hydrocarbons therefrom;
- (4) recovering said stripped liquid phase;
- (5) cooling said vapor phase separated in step (2) to condense liquid hydrocarbons contained therein;
- (6) separating said liquid hydrocarbons of step (5);
- (7) stripping said liquid hydrocarbons from step (6) with steam to remove dissolved low-boiling hydrocarbons therefrom; and
- (8) recovering said condensed hydrocarbons from step (7) having substantially improved color properties.

2. The process of claim 1 wherein step (2) is conducted at substantially the temperature and pressure conditions prevailing in step (1).

3. The process of claim 1 wherein the hydrofined effluent is partially condensed by cooling to separate said vapor phase from said liquid phase.

4. The process of claim 1 wherein said hydrofining conditions include a temperature of about 450 to 700° F., a pressure of about 125 to 500 p.s.i.g., and a space velocity of about 1 to 6 v./v./hour, and wherein hydrogen is introduced at a rate of about 20 to 5000 standard cubic feet per barrel of feed.

5. The process of claim 4 wherein said middle distillate feed has a boiling range of about 300 to 700° F.

6. An improved process for enhancing the color properties of hydrocarbon fractions which comprises:

- (1) subjecting a hydrocarbon feed boiling in the range of 300–700° F. to hydrofining at a temperature in the range of 450–700° F., a pressure in the range of 125–500 p.s.i.g. and a space velocity of 1–6 v./v./hr. in the presence of hydrogen and a hydrofining catalyst, wherein the hydrofining conditions are selected to maintain said fractions substantially in the vapor phase;
- (2) separating the effluent from step (1) into a liquid phase and a vapor phase predominantly containing said hydrocarbon fractions at the conditions recited in step (1);
- (3) stripping said liquid phase separated in step (2) at a pressure in the range of 125–500 p.s.i.g. with steam to remove dissolved low-boiling hydrocarbons therefrom;
- (4) recovering said stripped liquid phase;
- (5) cooling said vapor phase separated in step (2) to form a vaporous portion comprising hydrogen and hydrogen-containing products and a condensed liquid hydrocarbon portion predominantly containing said hydrocarbon fractions;
- (6) separating said condensed liquid hydrocarbon portion from said vaporous portion of step (5);
- (7) stripping said condensed hydrocarbon portion separated in step (6) with steam to remove dissolved low-boiling hydrocarbons therefrom; and
- (8) recovering said hydrocarbon fractions from step (7) having substantially improved color properties.

#### References Cited

##### UNITED STATES PATENTS

2,983,675	5/1961	Baxter et al.	208—212
3,011,971	12/1961	Slyngstad et al.	208—216
2,769,754	11/1956	Sweetser et al.	208—210
3,147,210	9/1964	Hass et al.	208—210

DELBERT E. GANTZ, Primary Examiner

G. J. CRASANAKIS, Assistant Examiner

U.S. Cl. X.R.

208—212