United States Patent Office 3,843,508 Patented Oct. 22, 1974

3,843,508

SPLIT FLOW HYDRODESULFURIZATION AND CATALYTIC CRACKING OF RESIDUE-CONTAINING PETROLEUM FRACTION

Raymond F. Wilson, Reese A. Peck, and Frank E. Guptill, Jr., Fishkill, N.Y., assignors to Texaco Inc., New York, N.Y.

No Drawing. Continuation-in-part of application Ser. No. 101,444, Dec. 24, 1970, now Patent No. 3,671,420, which is a continuation-in-part of application Ser. No. 811,604, Mar. 28, 1969, now Patent No. 3,607,723. This application Apr. 17, 1972, Ser. No. 244,863
The portion of the term of the patent subsequent to July 27, 1988, has been disclaimed
Int. Cl. C10g 23/02
U.S. Cl. 208—89 11 Claims

ABSTRACT OF THE DISCLOSURE

Residue-containing petroleum oils are converted into lighter products by a combination of split flow hydrodesulfurization to produce overhead and bottoms fractions of reduced sulfur content and catalytic cracking of the overhead and bottoms from the desulfurization in separate risers of a multiple riser catalytic cracking unit.

This application is a continuation-in-part of our copending application Ser. No. 101,444 filed Dec. 24, 1970, now U.S. Pat. 3,671,420 which in turn is a continuation-in-part of our application Ser. No. 811,604 filed Mar. 28, 1969, now U.S. Pat. 3,607,723.

This invention relates to the catalytic treatment of heavy hydrocarbon materials and more particularly to a process which produces substantially complete conversion of said heavy hydrocarbon materials to lower boiling hydrocarbons.

Motor fuel, diesel fuel and jet fuel are for the most part, the most valuable products obtained from petroleum. Consequently the petroleum industry is geared to produce maximum amounts of these products. To this end, crude petroleum is distilled to obtain these desired fractions and that portion of the distillate boiling above the desired fractions is subjected to hydrocracking or to catalytic cracking to convert it to lower boiling material.

However, the still residue is a heavy hydrocarbon oil rich in tar and asphalt and having a relatively high concentration of metals. Attempts to convert still residues such as a vacuum residuum into lighter materials by means of catalytic processes have not been particularly successful as the tar and asphalt present in the residue deposit on the catalyst producing a coke layer thereon preventing contact of the catalyst and oil. In addition in many cases the metals will deposit on the catalyst causing its deactivation. As a result, the most popular method for converting residua to lighter materials is coking, in which process the oil is heated and retained at elevated temperature until a substantial portion thereof is converted to coke and the balance to a lighter liquid. However, disposal of the coke so formed can present a problem. In fact, much of the still residue produced in petroleum refineries is sold as "residual fuel" but even this is no longer a suitable use because of its high sulfur content.

It is therefore an object of this invention to provide a process for the catalytic conversion of residue containing hydrocarbon oils into valuable lighter products. Accordingly, our invention provides a process for the conversion of a residue-containing petroleum fraction into lighter products which comprises maintaining in a hydrodesulfurization zone a first catalytic zone below and a second catalytic zone above a point of entry into said

hydrodesulfurization zone, introducing the residue-containing petroleum fraction through said point of entry into said hydrodesulfurization zone at a temperature between about 600 and 775° F. and a pressure between about 500 and 5000 p.s.i.g., introducing hydrogen into said first catalytic zone to flow upwardly countercurrent to a portion of said residue-containing petroleum fraction at a rate of at least 3000 s.c.f. of hydrogen per barrel of residue containing petroleum fraction sufficient to maintain liquid hydrocarbon in said second catalytic zone, separately recovering product from said first and second catalytic zones, catalytically cracking the overhead product from said second catalytic zone and separately catalytically cracking the bottoms from said first catalytic zone.

The process of our invention may be used for the treatment of residue-containing fractions such as atmospheric residua, vacuum residua, visbreaker bottoms, whole crude such as San Ardo Crude, shale oil, tar sand oil and the like.

It has now been found that substantial conversion of heavy hydrocarbon materials to lower boiling hydrocarbons can be accomplished in a split flow hydrodesulfurization process which comprises introducing a heavy hydrocarbon charge stock into a hydrodesulfurization catalyst zone, said catalyst zone comprising a first catalyst zone below and a second catalyst zone above the point of entry of the heavy hydrocarbon charge stock, introducing hydrogen into said first catalyst zone in countercurrent relationship to the downward flow of at least a portion of said heavy hydrocarbon charge stock, maintaining a lower boiling liquid in the second catalyst zone, recovering a high boiling effluent or bottoms from the first catalyst zone and recovering lower boiling hydrocarbons as overhead from the second catalyst zone.

In carrying out the process of this invention, the heavy hydrocarbon charge stock is introduced into a hydrodesulfurization catalyst zone herein defined to include a first catalyst zone in downflow relationship to the downward flow of the heavy hydrocarbon charge stock, a second catalyst zone above the point of entry of the heavy hydrocarbon charge stock and in upflow relationship to the lower boiling hydrocarbons which proceed from the first catalyst zone into the second catalyst zone. By the use of the term "downward flow" is meant that the heavy hydrocarbon charge stock proceeds in downflow relationship to the first catalyst zone. By the use of the term "above" in reference to the second catalyst zone is meant only that the second catalyst zone is in upflow relationship to the flow of the hydrogen containing gas and in upflow relationship to the volatile hydrocarbon and entrained liquid hydrocarbon which proceed from the first catalyst zone into a second catalyst zone. The word "above" is used to define a flow relationship with the first catalyst zone, which relationship provides for the flow of hydrogen, volatile hydrocarbons and entrained lower boiling liquid hydrocarbons from the first catalyst zone in countercurrent relationship with the downward flow of the heavy hydrocarbon charge stock into a second catalyst zone. Thus the second catalyst zone can be located directly in a space dimension above the first catalyst zone such as when the first and second catalyst zone are present in a vertical reactor with an intermediate point of entry for the heavy hydrocarbon charge stock. However, this invention contemplates that the second catalyst zone can be present as a separate reactor which is connected to the first reactor by conduit means, although it is preferred in carrying out the process of this invention to use a vertical reactor wherein the first catalyst zone and second catalyst zone and present in the same reactor. Within the first and second catalyst zone is a catalyst which has hydro-

desulfurization activity under process conditions of temperature, pressure and space velocity which are utilized during the process. In addition, the catalyst in the first catalyst zone can be either the same or different than the catalyst present in the second catalyst zone.

The hydrocarbon charge stock upon entry to the catalyst zone proceeds at least in part downwardly in downflow relationship to the first catalyst zone. Hydrogen is introduced into the first catalyst zone at or near the lower extremity and/or at intermediate points in said first catalyst zone in countercurrent relationship to the hydrocarbon flow through the first catalyst zone and in upflow relationship to the second catalyst zone, the volatile hydrocarbons and the lower boiling liquid hydrocarbons hereinafter referred to as liquid proceed into the second catalyst zone. The volatile hydrocarbons and the liquids which are present in the second catalyst zone proceed from the second catalyst zone and are recovered by conventional means such as by cooling of the hydrocarbon vapors and liquid. The hydrogen which proceeds from the second catalyst zone can then be recycled together with fresh hydrogen into the first catalyst zone. In addition, hydrogen optionally can be blended with the heavy hydrocarbon charge stock and introduced into the catalyst zone.

As stated above, liquid is maintained in the second catalyst zone. In general, a liquid is maintained in the second catalyst zone by the rate of introduction of hydrogen into the first catalyst zone by any of the means set forth above for the introduction of hydrogen. In order to maintain liquid in the second catalyst zone utilizing hydrogen, it has been found the hydrogen gas rates of at least 3000 s.c.f. per barrel of charge are required with rates of from 3000 s.c.f. per barrel up to about 25,000 s.c.f. per barrel being preferred in the first catalyst zone. The hydrogen need not be pure and gases containing more than about 65 volume percent hydrogen may be used. In this connection, the term "hydrogen" is also intended to include dilute hydrogen, reformer by-product hydrogen, hydrogen produced by the partial oxidation of hydrocarbon materials followed by shift conversion and electrolytic hydrogen.

The hold-up of the liquid hydrocarbon charge stock in the first catalyst zone can be varied somewhat by varying the upward flow of hydrogen. In general it is preferred to have high liquid hold-up, that is a hold-up of hydrocarbon charge stock with provides for maximum catalytic effectiveness for the desulfurization of the charge stock.

The lower boiling liquid which is maintained in the second catalyst zone is derived from the heavy hydrocarbon material, and in general is a lower boiling hydrocarbon which is present initially in the heavy hydrocarbon charge stock and/or which is formed during the process. In general the liquid material has a boiling point below 850° F. It is preferred that the liquid which is present in the second catalyst zone have at least about 90% by weight of the liquid boiling below 850° F. more preferably at least about 97% by weight boiling below 850° F.

The first stage of the process of this invention is utilized for the desulfurization of heavy hydrocarbon charge stocks which term is herein defined to mean conversion of a substantial portion of the sulfur present in the charge stock to hydrogen sulifide. The hydrodesulfurization conditions as to pressure, temperature and space velocity can be varied over a wide range, the conditions utilized being those which in combination produce substantial conversion of the sulfur in the charge stock to hydrogen sulfide.

The first and second catalyst zone conditions that are utilized in the split flow process of this invention are in general temperatures of from about 600° F. to about 775° F., preferably 625° F. to 750° F.; pressures of from about 500 to about 5000 p.s.i.g., preferably 1500 to 2000 p.s.i.g. and liquid hourly space velocities of from about 0.05 to about 10, preferably 0.25 to 2.5, volumes of feed per volume of catalyst per hour.

In general it is preferred to have approximately the same conditions in the first and second catalyst zones although the gas rates in the first and seccnd catalyst zones will differ depending upon the amount of hydrogen which is introduced with the heavy hydrocarbon charge stock into the catalyst zone and/or hydrogen consumed in the process. Thus hydrogen gas rates in the second catalyst zone may be different than the hydrogen rates in the first catalyst zone. In general the liquid hourly space velocity in the second catalyst zone will be greater than that in the first catalyst zone. In addition as in the case where the catalyst zones are not present in the same reactor, temperature and pressure can be different.

The catalyst utilized for the desulfurization of the aforementioned hydrocarbon charge stocks comprises an iron group metal alone or in conjunction with a Group VI metal, compounds and mixtures thereof, e.g. cobalt oxide and molybdenum oxide or nickel sulfide and tungsten sulfide on a refractory inorganic oxide support. The iron group metal may be present in an amount between about 1% and 15% preferably between 2% and 8% by weight based on the catalyst composite. The Group VI metal may be present in an amount between about 2 and 30% preferably between 4 and 20% by weight based on the catalyst composite. The catalyst support is, as mentioned above, a refractory inorganic oxidet such as silica, alumina, zirconia or magnesia or mixtures thereof. The support should be inert and should have substantially no cracking activity. A particularly suitable support is alumina containing minor amount, e.g., 2–14 wt. percent silica based on the catalyst composite.

The same or different catalysts may be used in each catalyst zone. Since the catalyst in the first zone comes into considerable contact with tar and residual components, it should have a surface area of at least 250 $m.^2/g.$, preferably 300–600 $m.^2/g.$ and a pore volume of at least 0.6 cc./g. preferably 0.6–1.0 cc./g.

Hydrogen is separated from the effluent from the second catalytic zone and if desired may be recycled for introduction with the charge or to the first catalytic zone with or without purification for the removal of compounds such as hydrogen sulfide and/or ammonia. Lower boiling hydrocarbons, e.g. those boiling up to about 525–550° F. may be also removed from the second catalytic zone effluent and the balance is subjected to catalytic cracking as is the effluent from the first catalytic stage. Since the hydrocarbon effluent from the second catalytic zone or overhead is higher in saturates than the effluent from the first catalytic zone or bottoms, they are subjected to different conditions of catalytic cracking. This is done effectively with a zeolite cracking catalyst in a fluid catalytic cracking unit comprising a reactor, a regenerator and at least two elongated reaction zones or risers where the reactor contains a dense phase and a dilute phase of the catalyst.

In the simplest embodiment of this invention, a fluid catalytic cracking unit with two risers is employed with the operating conditions in the risers including a temperature of 800–1150° F., conversion of 30–85 volume percent and space velocities in the overhead riser and the bottoms riser being 10–100 w./hr./w. and 50–200 w./hr./w/., respectively.

Both riser cracking and fluidized dense phase cracking may be employed.

In one embodiment the cracking of the overhead and the bottoms is restricted to the risers by discharging the effluent from both risers into the dilute phase of catalyst in the reactor vessel. The reactor vessel in this case is utilized as a disengaging space with substantially no cracking taking place therein.

In another embodiment, the overhead is subjected to both riser and dense phase cracking while the cracking of the bottoms is limited to its riser. The effluent from

the bottoms riser is discharged into the dilute phase of catalyst, the effluent from the overhead riser is discharged into the dense phase of catalyst and the vaporous reaction mixture from the overhead riser is passed through the dense phase of catalyst under catalytic cracking conditions effecting an additional conversion of 5–30 volume percent with the total per pass conversion of the overhead not exceeding 85 volume percent. By adjusting the operating conditions, the conversion in the overhead riser may be lower, equal to or higher than that in the bottoms riser.

In a further embodiment, the overhead is subjected only to riser cracking while the bottoms is cracked in both the riser and the dense phase of catalyst. The effluent from the overhead riser is discharged directly into the dilute phase of catalyst in the reactor vessel, while the effluent from the bottoms riser is discharged into the dense phase of catalyst and passed through this dense phase under catalytic cracking conditions effecting an additional conversion of 5–30 volume percent. The per pass conversion of the bottoms does not exceed 85 volume percent.

In another embodiment, both the overhead and the bottoms are subjected to both riser cracking and dense phase bed cracking by discharging the effluent from both risers into the dense phase of catalyst and passing them therethrough under catalytic cracking conditions to effect an additional conversion of 5–30 percent. In this embodiment the total conversion of all oils passing through the catalytic cracking unit does not exceed 85 volume percent.

In a preferred embodiment, the overhead is subjected only to riser cracking and the bottoms is subjected to both riser and dense phase cracking.

It is also contemplated that other materials may be fed to the fluid catalytic cracking unit. For example, a virgin gas oil may be introduced into the riser with the overhead and the unconverted oil which ordinarily is recycled to the cracking unit is introduced into a separate riser with the bottoms. In one of the more specific embodiments of our invention a crude oil is fractionated at atmospheric pressure to produce naphtha, kerosene, atmospheric gas oils and an atmospheric residuum, the atmospheric residuum is subjected to split flow hydrodesulfurization, the atmospheric gas oil is subjected to catalytic cracking, the overhead from the split flow hydrodesulfurization is combined with the atmospheric gas oil as fresh feed to the fluid catalytic cracking unit and the unconverted gas oil feed is combined with the bottoms from the split flow hydrodesulfurization and is catalytically cracked under conditions such that the conversion of the lighter material is at least as great as that of the heavier material and may be as much as 30% more.

The catalyst employed in the instant invention comprises a large pore crystalline aluminosilicate customarily referred to as a zeolite and an active metal oxide, as exemplified by silica-alumina gel or clay. The zeolites employed as cracking catalysts herein possess ordered rigid three-dimensional structures having uniform pore diameters within the range of from about 6 to about 15 A. The crystalline zeolitic catalysts employed herein comprise about 1 to 25 wt. percent zeolite, about 10 to 50 wt. percent alumina and the remainder silica. The preferred zeolite is decationized zeolite Y wherein at least a substantial portion of the original alkali metal ions have been replaced with such cations as hydrogen and/or metal or combination of metals such as barium, calcium, magnesium, manganese or such rare earth metals, for example, cerium, lanthanum, neodymium, praseodymium, samarium and yttrium.

As contemplated herein the overhead and bottoms are introduced into elongated reaction zones which are operated to effect a lower conversion of the bottoms stream. In its simplest form, a two riser fluid catalytic cracking unit is employed. The operating conditions for both the overhead riser and the bottoms riser include an operating temperature of 800–1150° F., preferably 840–1000° F. and a conversion per pass of 30–85 percent, preferably 40–75 percent. Other operating conditions within the risers include a residence time of 2–20 seconds, preferably 3–10 seconds and a vapor velocity of 15–50 ft./sec., preferably 20–40 ft./sec. The space velocity in the overhead riser is 10–100 w./hr./w., preferably 40–90 w./hr./w. and the space velocity in the bottoms riser is 50–200 w./hr./w., preferably 75–150 w./hr./w. The conversion per pass in the bottoms riser is 0–30 percent lower than the conversion in the overhead riser with the overall conversion in the overhead riser not exceeding 85 volume percent.

Where the embodiment employed includes additional cracking of either effluent in the dense phase of catalyst in the reactor the operating conditions within the dense phase include a temperature of 800°–1150° F., a vapor velocity of 0.5–4 ft./sec., preferably 1.3–2.2 ft./sec. and a space velocity of 1–40 w./hr./w., preferably 3–25 w./hr./w. The vaporous reaction products from a riser which passes through the dense phase of catalyst obtains a further conversion of 5–30 volume percent.

In the operation of our process it has been found desirable to operate the hydrodesulfurization stage under such conditions that the end point of the overhead or second catalytic zone effluent is about 850° F. and correspondingly the initial boiling point of the bottoms or first catalytic zone effluent is about 850° F. Of course it will be appreciated that because of the solubility of hydrocarbons in heavier hydrocarbons there is no sharp demarcation and the boiling ranges will overlap.

One of the features of our process is that our split flow operation will effect greater desulfurization than will a conventional process in which both the charge and hydrogen pass downwardly through the catalyst bed. Another feature is that the overhead from the split flow desulfurization stage is higher in saturates than is the bottoms product. In conventional downflow desulfurization there is only one product. Furthermore, even if the product from conventional downflow hydrodesulfurization is fractionated, there is no aromatic-saturate separation equivalent to that obtained by the split-flow desulfurization stage of our process.

The fact that the overhead and bottoms of the split flow desulfurizer have different characteristics means that each can be cracked separately under conditions most suitable for that fraction. It has also been found that the overhead from the split flow desulfurization of atmospheric residuum behaves like virgin gas oil when subjected to catalytic cracking whereas the split flow desulfurizer bottoms is more aromatic and requires more severe cracking conditions. In this respect the bottoms product resembles unconverted gas oil which is ordinarily reclycled to the catalytic cracking unit.

Another feature of our invention is that by introducing that bottoms product into the catalyic cracking unit, considerably more carbon than usual is introduced into the catalyst bed thereby permitting greater deposition of carbon on the catalyst which in turn permits operation with a regenerated catalyst having a carbon level up to about 4.0 weight percent. By operating in this manner it is possible to burn off the deposited carbon from the catalyst under carefully controlled conditions to provide a catalyst containing from 0.2 to 2.5 weight percent retained coke and also to have the catalyst at a temperature between about 1100 and 1250° F. for reintroduction into the catalytic cracking zone. The presence of the retained carbon on the regenerated catalyst serves to prolong the life of the catalyst as the metallic components of the bottoms product become incorporated in the carbon layer with slight effect on the activity and selectivity of the catalyst.

Another feature of our process is that the more easily cracked feed to the cracking stage can be introduced

separately from and reacted under less severe conditions than the more difficultly cracked material thereby avoiding overcracking and the undesirable production of gases obtained in conventional processes where the feed is a single mixture or where the only difference between two or more feds lies in the boiling range and not in the type of hydrocarbons in the feeds.

The following example is for illustrative purposes only and should not be considered as limiting the invention in any manner.

EXAMPLE I

In this example, a South Louisiana reduced crude having an API gravity of 21.1°, a sulfur content of 0.48 wt. percent and a Conradson Carbon Residue of 4.14 wt. percent is hydrodesulfurized using the countercurrent split flow technique by being introduced at the mid-point of a bed of pelleted catalyst containing 2.8% Ni. 9.9% Mo, 2.5% silica and the balance alumina and having a surface area of 312 m.²/g., a pore volume of 0.66 cc./g. and an average pore diameter of 84.6 A. Reaction conditions for the desulfurization are tabulated below:

TABLE I

Temperature, ° F.	750
Pressure, p.s.i.g.	1700
Feed rate, Vo./hr./Vc.	1.1
H_2 rate, s.c.f.b. (with feed)	725
H_2 rate, s.c.f.b. (countercurrent)	7500

Hydrogen, light gases and naphtha are removed from the overhead with the balance, boiling range 360–745° F., being cracked in a riser of a fluid catalytic cracking unit at a temperature of 860° F. and bottoms from the countercurrent split flow hydrodesulfurization being subjected to cracking in a riser and dense bed at a temperature of 940° F. to obtain maximum conversion to naphtha using a catalyst containing 2.0 wt. percent cerium, 0.93 wt. percent lanthanum, 18.0 wt. percent decationized zeolite Y, 0.94 wt. percent sodium, 34.1 wt. percent alumina and the balance silica. The yields tabulated below are in terms of volume percent basis charge to the fluid catalytic cracking unit.

TABLE II

C_3	5.64
C_3=	6.03
iso-C_4	9.89
n-C_4	2.94
C_4=	4.51
Debutanized naphtha	66.22
Gas oil (400–714° F.)	15.0

The gasoline product has an octane rating better by several units than would be expected by catalytically cracking a virgin gas oil from the same charge under substantially the same conditions. Octane ratings for the 100° F.–400° F. fraction of the product and other data appear below:

TABLE III

Research octane No., clear	94.6
Research octane No. (+3 cc. TEL/gal.)	102.9
Motor octane No., clear	83.8
Motor octane No., (+3 cc. TEL/gal.)	89.9
Sulfur, wt. percent	0.018
Paraffins, vol. percent	35.1
Olefins vol. percent	20.9
Naphthenes, vol. percent	11.5
Aromatics, vol. percent	32.5

The above example represents one specific embodiment of our invention. Obviously, various modifications of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be made as are indicated in the appended claims.

We claim:

1. A process for the conversion of a residue-containing petroleum fraction having an initial boiling point of about 850° F. into lighter products which comprises maintaining in a hydrodesulfurization zone a first catalytic zone below and a second catalyst zone above a point of entry into said hydrodesulfurization zone, each of said catalytic zones containing a hydrodesulfurization catalyst comprising an iron group metal hydrogenation component on a refractory inorganic oxide support of substantially no cracking activity, the catalyst in said first catalytic zone having a surface area of from 250 to 600 m.²/g. and a pour volume of from 0.6 to 1.0 cc./g., introducing the residue-containing petroleum fraction through said point of entry into said hydrodesulfurization zone, maintaining said first and said second catalytic zone at a temperature between about 600 and 775° F. and a pressure between about 500 and 5000 p.s.i.g., introducing hydrogen into said first catalytic zone to flow upwardly serially through said first and said catalyst zones and countercurrent to a portion of said residue-containing petroleum fraction at a rate of at least 3000 s.c.f. per barrel of residue-containing petroleum fraction sufficient to maintain liquid hydrocarbon in said second catalytic zone, separately recovering product from said first and second catalytic zones, catalytically cracking the overhead product from said second catalytic zone and separately catalytically cracking the bottoms from said first catalytic zone.

2. The process of claim 1 in which the overhead is catalytically cracked in one riser of a multiple riser catalytic cracking zone and the bottoms product is cracked in another riser of said multiple riser catalytic cracking zone.

3. The process of claim 2 in which a virgin gas oil is also introduced into said one riser and catalytically cracked with said overhead.

4. The process of claim 3 in which the product of the catalytic cracking of said overhead and said virgin gas oil is separated into a naphtha fraction and a fraction boiling above the naphtha range and the latter is catalytically cracked with said bottoms product.

5. The process of claim 3 in which naphtha and kerosene fractions are recovered from the catalytic cracking product of said virgin gas oil and said overhead and that portion of the product boiling above the kerosene range is catalytically cracked with said bottoms product.

6. The process of claim 2 in which the bottoms product after being at least partially catalytically cracked in said riser, is withdrawn therefrom and subjected to additional cracking in the dense phase of a fluidized cracking catalyst bed.

7. The process of claim 2 in which said one riser is operated at a temperature between about 800 and 1000° F. and said other riser is operated at a temperature between about 850 and 1100° F.

8. The process of claim 2 in which the catalyst in each of said risers contains between about 0.5 and 4.0 weight percent carbon.

9. The process of claim 1 in which the surface area is between 300 and 500 m.²/g. and the pore volume is between 0.6 and 0.8 cc./g.

10. The process of claim 2 in which naphtha and kerosene are recovered from the catalytic cracking product of the overhead and that portion of the product boiling above the kerosene range is combined with and catalytically cracked with said bottoms product.

11. The process of claim 3 in which the catalyst in said risers contains between about 0.5 to 4.0 weight percent carbon.

(References on following page)

References Cited

UNITED STATES PATENTS

3,595,779	7/1971	Peck et al.	208—89
3,425,810	2/1969	Scott, Jr.	208—89
3,124,526	3/1964	Butlet et al.	208—89
2,962,435	11/1960	Fleck et al.	208—120
3,168,461	2/1965	Russell et al.	208—89
3,617,501	11/1971	Eng et al.	208—89

3,355,380	11/1967	Luckenbach	208—164
3,679,576	7/1972	McDonald	208—164

DELBERT E. GANTZ, Primary Examiner

G. J. CRASANAKIS, Assistant Examiner

U.S. Cl. X.R.

208—210, 76, 80