

July 10, 1962

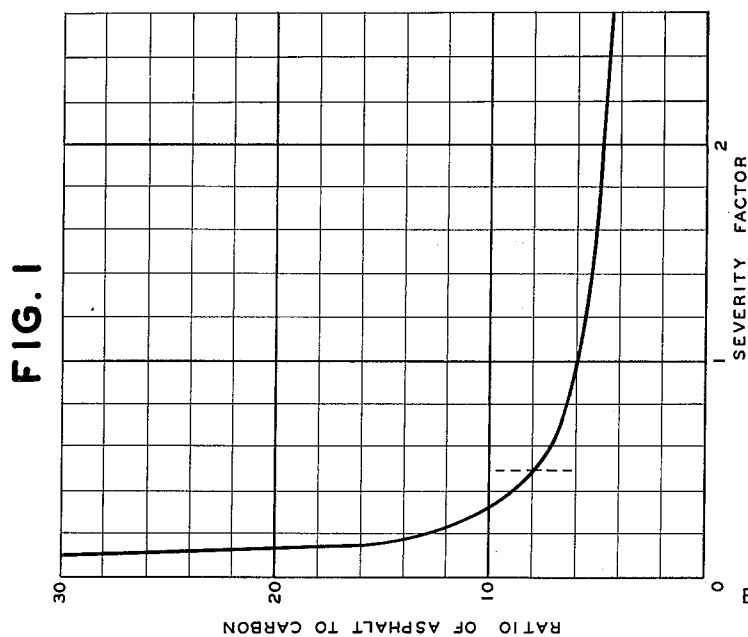
M. F. NATHAN ET AL

3,043,769

DESTRUCTIVE HYDROGENATION OF HEAVY HYDROCARBON

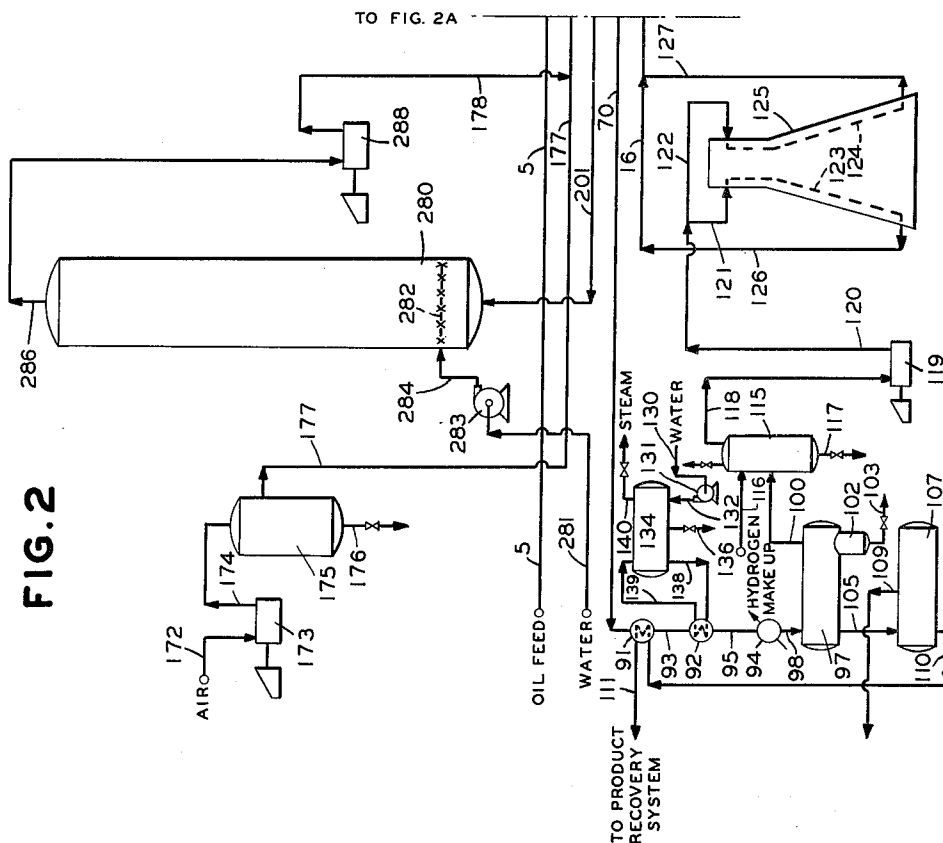
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2 Sheets-Sheet 1



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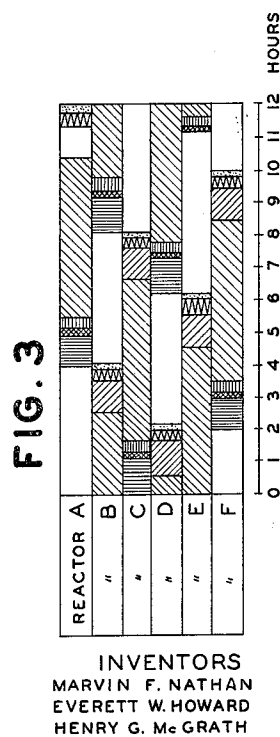
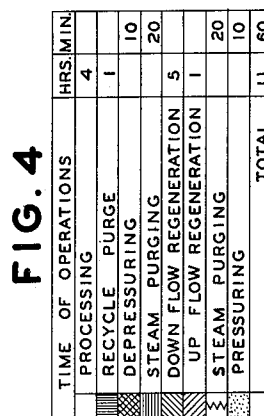
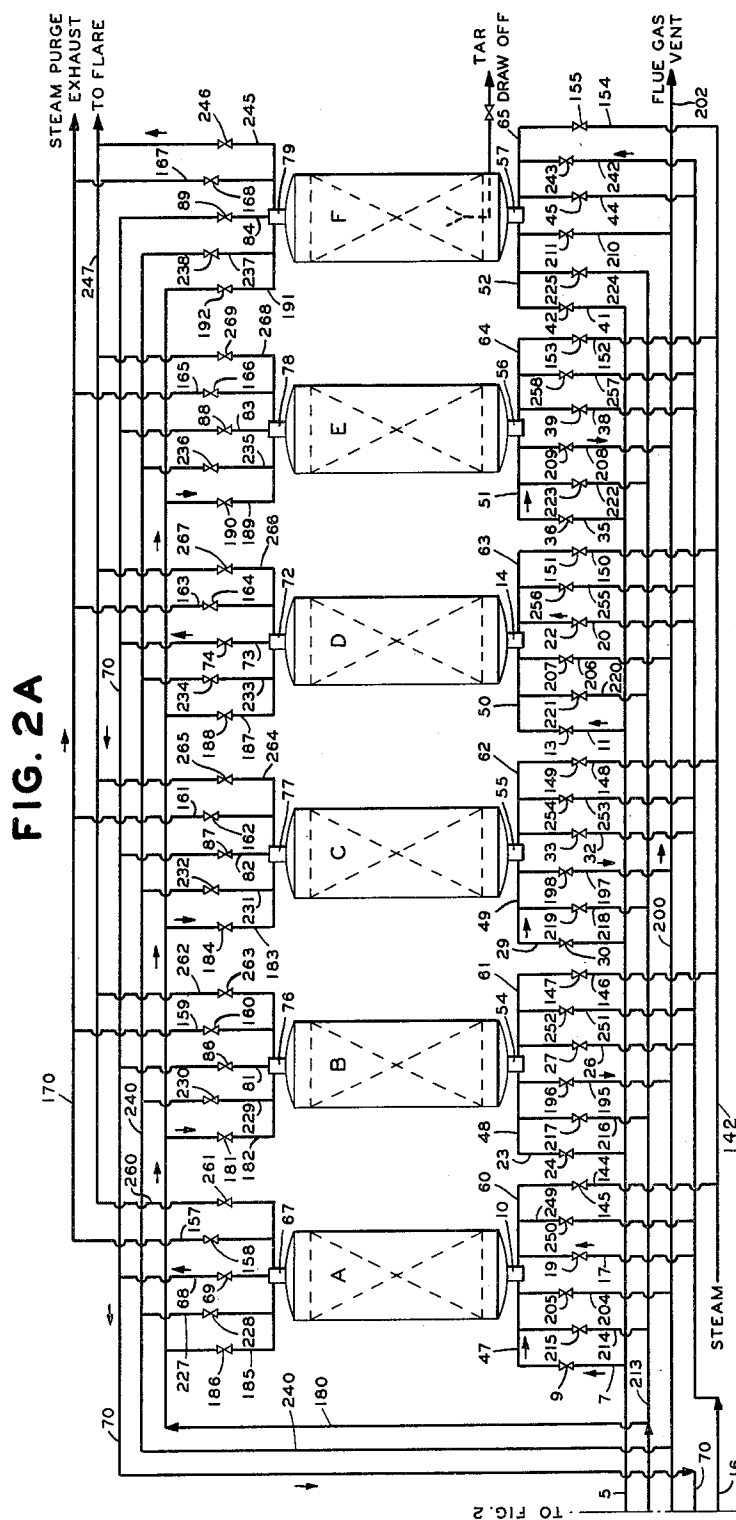
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DESTRUCTIVE HYDROGENATION OF HEAVY HYDROCARBONS

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5 Claims. (Cl. 208-112)

The present invention relates to an improved process for cracking under hydrogen pressure, and more particularly, it pertains to a method of cracking heavy or residual oils under hydrogen pressure whereby a minimum production of carbon and normally gaseous products is obtained and a suitable feed material for catalytic operations is produced.

Residual oils in petroleum refineries are distress stocks in that they are not very satisfactory as feed materials for cracking operations by reason of metal contamination of the catalyst and the simultaneous undesired production of carbon and normally gaseous products which represents an economic loss. It has been suggested that such materials be subjected to a coking operation whereby gasoline and other product materials are produced, however, this process is not considered too satisfactory for commercial exploitation, because of the poor anti-knock quality of gasoline product and the high yield of carbon.

Another previously suggested technique involves conventional catalytic cracking of this material, however, this method is not entirely satisfactory because of the high carbon yields and the adverse effect of the feed stock on catalyst life. It has also been proposed that residual oils be cracked under hydrogen pressure in order to overcome some of the disadvantages enumerated above, and it was found that while this process had advantages, the results were not sufficient to justify commercial application.

Upon further investigation, it was discovered that prior workers were emphasizing factors in the method of cracking under hydrogen pressure which did not serve for the best efficiency nor economical interest. For example, prior workers emphasized in their work the use of operating conditions which would produce a maximum yield of gasoline. Invariably, this method of operation results in converting an uneconomical quantity of feed material to carbon and normally gaseous products and in producing a grade of gasoline which is not as good as the product from a catalytic cracking operation. By extensive investigation, it was discovered by use, that cracking under hydrogen pressure should be operated under mild conditions to produce little or no gasoline such that a small amount of feed material is converted to carbon and gas, and an excellent feed stock for catalytic cracking is produced. By operating in this manner, the amount of gasoline produced is small; however, this is an advantage, because cracking under hydrogen pressure is an expensive way of making gasoline, and any gasoline made may require further processing to improve the quality thereof. By means of the present invention, the final gasoline product is made by the efficient and economical method of conventional catalytic cracking.

An object of this invention is to provide an improved method for cracking residual oils under hydrogen pressure.

Another object of this invention is to provide a combination process in which residual oil is cracked under hydrogen pressure to produce a feed stock for a catalytic cracking operation.

Still another object of this invention is to crack residual oils under hydrogen pressure to produce a high yield

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of feed stock for catalytic cracking operations and a low yield of carbon and normally gaseous products.

Other objects and advantages of this invention will become apparent from the following description and explanation thereof.

By means of the present invention, a residual oil is cracked under hydrogen pressure in the presence of a suitable catalyst and under cracking conditions including a severity factor of not more than about 0.50. The severity factor is defined hereunder as the quotient of dividing the catalyst to oil ratio by the volumetric space velocity. The catalyst to oil ratio in this invention is the volumetric ratio of catalyst to oil, on an hourly basis. Ordinarily, the catalyst to oil ratio is used only to describe an operating condition in moving fluid bed systems, however, for the purposes of this specification and the appended claims, a superficial catalyst to oil ratio is also used for a fixed bed system, and it is determined by taking the reciprocal of the product of the reaction period or cycle in hours and the volumetric space velocity.

The best application of this invention is to utilize as feed stock a material which is commercially unattractive for any of the gasoline producing processes, for example, catalytic cracking, thermal cracking, vacuum distillation, etc. Generally, such a material has an API gravity of up to about 20, however, this invention has particular applicability for processing feed stocks having an API gravity of from about 1 to about 13; and which has an unusually high carbon residue, generally, more than about 0.6% by weight, more usually, about 5 to 30% by weight. Another method of indicating this characteristic of the feed material is the asphalt content, and it can be from about 2 to 60% by weight, more usually about 15 to 50%. In refining practice, the crude oil is separated into several fractions, one of which constitutes the feed stock for conventional catalytic cracking, and it has an end point in the range of about 850° to about 1025° F. The higher boiling fraction is the residual oil, and it has an initial boiling point which varies with the end point of the feed material for the conventional cracking operation. This residual oil has a high coking tendency by reason of the high molecular weight compounds it contains and the asphaltic nature of them. Another characteristic of the feed stock for this invention is the sulfur content, which is usually higher than any other fractions separated from the crude oil. In the case of Mid-Continent crudes, the sulfur content is relatively low as compared to West Texas crudes, and for the purpose of this invention, the sulfur content is at least about 0.1% by weight, more usually, about 0.5 to 6% by weight. Specific examples of residual oils for use in this invention are reduced crudes representing up to about 40% of the total crude, more usually, not more than about 25% on a volumetric basis; although the best application of this invention is with regard to, for example, vacuum tar; thermal cracking tar; fuel oil; etc. It should be understood, however, that in the case of very heavy crude oils, the reduced crude may represent up to about 70 to 80% of the entire material and therefore, the gravity of the reduced crude is the controlling feature.

The residual oil is subjected under reaction conditions to a temperature which is suitable for effecting mild cracking reactions. The purpose is to convert residual oil compounds to catalytic cracking feed stock or gas oil with a relatively small production of gas, gasoline and coke as possible, and the production of an asphalt product which is suitable as a recycle stock for more production of gas oil. By means of the conditions employed in this invention, the feed stock is selectively cracked to the desired products. The feed stock to be used for conventional catalytic cracking is considered as having an

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initial boiling point of between about 575° to about 700° F. and an end point of between about 850° to about 1025° F. The product boiling above the gas oil is the asphalt fraction or product. The temperature at which cracking under hydrogen pressure is effected lies between about 675° and about 925° F., preferably about 750° to about 875° F. Higher temperatures tend to produce normally gaseous products at a faster rate than is desired, hence, they are not preferred; whereas lower temperatures than the minimum given above may result in an undesirably slow rate of reaction. The total reaction pressure is selected primarily on the basis of providing a desired hydrogen partial pressure. Accordingly, the pressure varies from about 50 to about 2500 p.s.i.g., more usually, about 500 to about 1500 p.s.i.g. With regard to reaction pressure, it should be noted that a substantial part of the feed stock may tend to exist in the liquid state under reaction conditions. It is preferred, however, for a fixed bed system, to effect the reaction in the liquid phase or in a mixed phase of vapor and liquid. In the fixed bed operation a non-fluid catalyst is employed by reason that a substantial amount of reactants can exist in the liquid state under reaction conditions. Such a mode of operation makes possible the production of large quantities of a heavy product fraction or asphalt boiling in essentially the same range as the residual oil feed, and this asphalt product has an API gravity falling within the range specified above for the residual oil feed. It should be understood that the present invention can be practiced as a fluid system, employing either the fixed or moving bed technique. In a severe operation, the quantity of such heavy product material may not be more than about 10% by volume of the feed; whereas in the practice of this invention, the yield of this material is usually at least about 35% or at least 45% and up to about 70% by volume, based on residual oil feed. This indicates the essential difference between our invention and a severe operation. Consequently, the heavy product or asphalt fraction which boils above the feed stock for the conventional catalytic cracking operation can be recycled to the reaction zone until all or part of the material is converted to lower boiling products and/or carbon. The recycle ratio, measured as parts by weight of product boiling above the catalytic cracking feed stock to parts by weight of residual oil feed, on the same time basis, is about 0.1 to 5, more usually, about 0.25 to 2. It is intended that all or part of the highest boiling product fraction be recycled to the reaction zone.

The reaction is conducted under hydrogen pressure in order to minimize carbon formation, produce a product of high saturation and containing a fraction having good characteristics as feed stock for catalytic cracking operations and a fraction which is not very refractory for re-processing, etc. To effect this purpose, hydrogen is supplied to the reaction zone as a pure gas or as a hydrogen containing gas having about 40 to 95% by volume of hydrogen. The hydrogen rate is measured as the standard cubic feet (60° F. and 760 mm.) per barrel of feed (1 barrel is equal to 42 gallons), s.c.f.b., and it can vary from about 500 to about 50,000 s.c.f.b., more usually, about 2500 to about 30,000 s.c.f.b.

The rate of charging residual oil to the reaction zone is measured on a relative basis to the volume of catalyst which is present therein. This is termed as the volumetric space velocity, and it is measured as the cubic feet of liquid feed charged to the reaction zone on an hourly basis per cubic foot of catalyst present therein. The volumetric space velocity is an important factor for measuring severity, although, in the present case, by itself, it is not as reliable as the severity factor. The volumetric space velocity varies from about 0.05 to about 10, more usually, about 0.25 to about 2.5, for the purpose of this invention. The volumetric space velocity includes the recycle oil rate.

Since the present invention can be operated as a fixed

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bed system, a superficial catalyst to oil ratio, on a volumetric basis, is employed for indicating severity. This superficial catalyst to oil ratio is calculated as the reciprocal of the product of the reaction period in hours and the volumetric space velocity. The reaction period is important, because in a fixed bed system, the activity of the catalyst declines with use, consequently, the longer the reaction period, the lower the catalyst activity. The importance of the volumetric space velocity was described above. In the practice of this invention, the catalyst to oil ratio (to be understood as including the superficial and actual catalyst to oil ratio) varies from about .001 to 4, more usually, about 0.1 to 1. The reaction period is also important, and it can vary from about 0.5 to 200 hours, more usually, about 2 to 150 hours. The required severity for the operation of our process is best determined by means of the severity factor, which is calculated in accordance with the following equation:

$$S.F. = \left(\frac{1}{(V.S.V.)(T)} \right) \frac{1}{(V.S.V.)}$$

"T" represents the reaction period in hours and "V.S.V." is the volumetric space velocity ($V_o/hr./V_c$). To produce the effects desired in this invention, the severity factor is not greater than about 0.50, more usually, about 0.05 to 0.5. It is shown hereinafter that by operating within the defined severity factor, the ratio of asphalt (product boiling above fraction used as feed for catalytic cracking) to carbon is very satisfactory for commercial use. The carbon yield is proportional to the normally gaseous product yield, hence, if the carbon yield increases, there is a similar effect in the gas yield. Further, by operating within the severity range of this invention, the yield of gasoline and furnace oil is substantially lower than is obtained by conventional methods of operation. There is a break point in the relative yields of the various products and this is best illustrated by the ratio of the asphalt product yield to the carbon yield. As the asphalt yield increases, the yields of carbon, gas, gasoline and furnace oil decreases, whereas the yield of gas oil which is to serve as catalytic cracking feed stock declines relatively little. Since the carbon represents an economic loss, the efficiency of operation for the purposes of this invention can be measured as the ratio of asphalt product to carbon. The greater the yield of asphalt, the smaller the loss of feed as carbon and normally gaseous material and since the gas oil yield varies relatively little, the conditions are chosen to produce large quantities of asphalt for subsequent recycle. Cracking lighter product fractions than residual oil under hydrogen pressure to produce gasoline is much more expensive than by conventional catalytic cracking. One reason for first treating the residual oil by means of this invention before charging the gas oil fraction or product to conventional catalytic cracking, is to avoid the great harm which is done to catalyst activity by the residual oil in conventional operations. Hydrogen pressure suppresses such effects to a significant extent, consequently, the present process is advantageous from this standpoint. Further, the coke yield in conventional cracking of residual oils is greater than in the method of this invention, because hydrogen pressure suppresses coke formation.

The main aspect of this invention is concerned with cracking under hydrogen pressure to produce feed stock for conventional catalytic cracking. A suitable feed stock for conventional catalytic cracking does not contain more than about 0.6% carbon residue, otherwise there may be serious adverse effects on catalyst activity. Another disadvantage in using residual oils containing more than about 0.6% carbon residue is the excessive coke production. Accordingly, in the practice of this invention, gas oil product to be used as feed for catalytic cracking operations should contain not more than the optimum

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amount of carbon residue. At present, this value is 0.6% by weight carbon residue, however, in the event that improvements in catalytic cracking permit the use of higher carbon residue in the feed, then it is intended to adjust the operation of this invention in order to provide a higher limit of carbon residue.

As a result of cracking under hydrogen pressure, the catalyst becomes contaminated with carbon or carbonaceous material which lowers the activity temporarily. The catalyst activity can be revived by burning the carbonaceous deposit with an oxygen containing gas, e.g., air, oxygen, diluted air containing 2 to 15% of oxygen by volume, etc., at a temperature of about 600° to 1250° F., more usually, about 950° to about 1200° F. The regeneration can be conducted at atmospheric pressure or at superatmospheric pressure as within the range mentioned above for the reaction. The quantity of oxygen containing gas used and the length of regeneration cycle depend upon the carbonaceous content of the catalyst. Generally, in a fixed bed system, the regeneration cycle is about 0.5 to about 50 hours, more usually, about 2 to 24 hours. Following the reaction cycle, the catalyst in the processing zone can be depressured; purged with inert gas such as, for example, steam, flue gas, carbon dioxide, nitrogen, etc.; and then subjected to regeneration treatment. Following regeneration, in some cases, it is desirable to precondition the catalyst with a hydrogen containing gas. This is particularly true of the dehydrogenation-hydrogenation types of catalysts.

The catalyst employed in this process is one which can possess cracking activity to a small extent, or this catalyst property can be predominant in conventional cracking catalysts. Generally, for the purposes of this specification and the appended claims, a cracking catalyst is one which possesses activity for cracking reactions to the extent suited for the present invention, and this can be at least about 5 or about 10% of the cracking activity possessed by a conventional silica-alumina cracking catalyst having a $D+L$ activity of about 45. The various types or groups of catalyst are many, including the silica containing cracking catalysts in which the silica varies from about 0.5 to 100% of the total catalyst, on a weight basis. In the type of catalyst used for conventional cracking, the silica content varies from about 20 to about 95% by weight of the total catalyst. Examples of silica containing catalysts are silica-alumina, silica-magnesia, silica gel, pumice, kieselguhr, fuller's earth, silica-zirconia, silica-boria, etc. Another group of catalysts are the alumina containing catalysts in which the alumina content varies from about 0.1 to about 100% by weight of the total catalyst. Examples of these catalysts are alumina gel or activated alumina, alumina-magnesia, alumina-boria, bauxite, Super-Filtrol, clays, etc. Another group of catalysts are those which are better known for their hydrogenation and/or dehydrogenation properties, including the compounds of elements of groups V and VI of the periodic table, notably the left hand elements of group VI in the form of the oxide and/or sulfide. These catalysts can be combined with compounds of group VIII metals having an atomic number not greater than 28, particularly the oxides and/or sulfides of these metals. Examples of catalysts coming within the definition of this latter group are molybdenum oxide-alumina, chromium oxide-alumina, tungsten oxide-alumina, tungsten oxide-nickel oxide-alumina, vanadium oxide-alumina, cobalt molybdate-alumina, tungsten sulfide-nickel sulfide-alumina, molybdenum sulfide-nickel sulfide-alumina, nickel on alumina, etc. The catalytic element constitutes about 0.1 to about 25% by weight of the total catalyst, and the carrier material can be materials other than alumina such as, for example, silica, silica-alumina, silica-magnesia, zinc spinel, bauxite, Super-Filtrol, etc.

Conventional catalytic cracking is familiar to those skilled in the art, and it includes such known processes as fluid catalytic cracking, Houdrifiow or the Houdry proc-

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ess, Thermoform catalytic cracking, Cycloversion, etc. These processes include moving and fixed beds using a fluid or non-fluid technique. Generally, a temperature of about 800° to about 1025° F. is used, more usually, 900° to about 1000° F., and the pressure varies from about one atmosphere to about 100 p.s.i.g. The weight space velocity, measured as the pounds per hour of liquid feed charged to the reaction zone per pound of catalyst present therein, varies from about 0.05 to 10, more usually, about 0.1 to about 3.0. In a moving bed system, the catalyst to oil ratio, on a weight basis, varied from about 0.5 to 20, more usually, about 2 to 10. The catalyst employed usually comprises the silica containing type, and it contains about 15 to about 100% silica. Examples of catalysts are silica gel, bauxite, Super-Filtrol, bentonite and montmorillonite clays, synthetic silica-alumina, silica-boria, silica-magnesia, silica-zirconia, etc. The silica-alumina containing catalysts are used extensively, and they contain about 15 to about 95% silica, based on the total weight of catalysts.

In another aspect of this invention, the total crude is first fractionated under atmospheric pressure to separate various straight run fractions as gasoline, naphtha, kerosene, gas oil, reduced crude, etc. The gas oil, all or part is utilized as diesel oil or as feed to a conventional catalytic cracking unit for the production of gasoline. The C_3 and C_4 unsaturated hydrocarbons produced in the catalytic cracking unit are charged to a catalytic polymerization unit, such as one using copper pyrophosphate or phosphoric acid as catalyst, to produce additional quantities of gasoline. The straight run naphtha is charged to a hydroforming unit which utilizes molybdenum oxide or chromia-alumina catalyst or platinum on alumina. The system is operated to effect a net production of hydrogen in a manner well-known to those skilled in the art, and it is a particular advantage in this invention to use the net hydrogen produced as feed in the cracking under hydrogen pressure operation. This is particularly true for Hydroformers using platinum catalysts, because the normally gaseous product contains about 80-90% hydrogen by volume. The reduced crude fraction comprising about 20 to about 60% by volume of the total crude is charged to a vacuum flashing or distillation unit. The overhead distillate from the vacuum unit is charged to the conventional catalytic cracking unit for gasoline production. The bottom fraction comprises about 5 to 25% by volume of the total crude and has an API gravity of about 1 to 13. This very heavy fraction is charged to the cracking under hydrogen pressure unit or hydrocracking unit for the production of feed stock for the conventional catalytic cracking unit, in accordance with the method of the present invention. The normally gaseous product from the hydrocracking unit is charged to the catalytic polymerization unit disclosed above. The normally liquid product from the hydrocracking unit can be charged directly to the atmospheric topping unit wherein straight run fractions are separated from the total crude for similar treatment. The feed stock for conventional cracking, produced in the hydrocracking unit, along with the asphalt product is processed through the vacuum flashing unit. A small part of the asphalt product, constituting about 1 to 15% by volume of the total asphalt product, can be withdrawn from the reactors as a fuel oil product. The recycled asphalt product and straight run vacuum tar are charged to the hydrocracking unit. Alternatively, the normally liquid product from the hydrocracking unit can be preliminarily treated to effect a separation of asphalt product under atmospheric pressure conditions, and this asphalt product is charged to the vacuum flashing unit to insure complete separation of the feed stock for conventional cracking or gas oil from the asphalt material. Alternatively, all or part of the straight run kerosene, without or with all or part of the cycle oil fraction from the conventional catalytic cracking unit can be charged to a thermal cracking unit for additional pro-

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duction of gasoline. The processes or units discussed above are well-known to those skilled in the art, hence, there is no need to discuss them herein with any degree of particularity. In the event that the quantity of hydrogen supplied to the hydrocracker from the hydroformer unit is not sufficient for hydrocracking needs, it is contemplated using a hydrogen unit involving reforming of methane or refinery gas with steam and the water gas shift reaction with steam.

For the purpose of evaluating this invention, a feed stock comprising vacuum tar, having the properties given below in Table I was processed in accordance with the conditions given in Table II. The results obtained are also reported in Table II. The catalyst used in these runs comprised 7.3% tungsten oxide, 2.7% nickel oxide and the remainder alumina, on a weight basis.

Table I

° API gravity	5.8
Viscosity, SUV, @ 130° F.	10346
Color, ASTM	8+D
Sulfur, wt. percent	5.45
Carbon residue, percent	19.8

Table II

Run No.	1	2	3	4	5
Temperature, ° F.	810	840	803	836	794
Pressure, p.s.i.g.	1,000	1,000	1,000	1,000	1,000
Space Velocity, Vol./hr./Vol.	0.31	0.60	0.68	1.45	0.68
Reaction Period, Hrs.	4	4	4	4	24
H ₂ rate, s.c.f.b.	18,000	24,000	18,000	8,000	19,000
Severity Factor	2.6	0.7	0.47	0.12	0.09
Yields (Basis Feed):					
Gasoline, IBP-410° F., Vol. Percent.	27.0	23.0	12.0	10.0	6.0
Furnace Oil, 410-670° F., Vol. Percent.	41.4	32.0	19.3	17.0	12.5
Gas Oil, 670-950° F., Vol. Percent.	27.3	24.0	21.1	21.0	20.0
Asphalt, 950° F., Vol. Percent.	4.1	21.0	47.7	54.0	61.4
Carbon, Wt. Percent.	6.4	3.5	2.4	1.4	0.6
Dry Gas, Wt. Percent.	6.4	5.2	1.5	1.8	0.9
Sulfur eliminated, Wt. Percent.	5.1	4.5	3.8	2.7	2.5

¹ C₇-C₃ hydrocarbons.

From the data presented in Table II, it can be seen that the yield of gas oil does not vary appreciably with different severity of operation conditions, but the quantity of asphalt varies widely. As the asphalt yield increases, the quantities of gasoline, furnace oil, carbon and dry gas decrease, hence, this product can serve as a means of indicating the severity of an operation. Since the carbon and dry gas represent an economic loss in the process, it is desirable to operate the present invention within the range defined by a sharp break in the ratio of asphalt to carbon. In this regard, a correlation of these two factors is given in FIGURE 1 of the attached drawings, and it is noted therefrom that the present invention should be operated with a severity factor not greater than about 0.5. Operations in which the severity factor is less than 0.5 result in a relatively high production of asphalt, however, the carbon, dry gas, gasoline and furnace oil yields are low. The asphalt can be recycled in any quantity desired to produce additional quantities of gas oil at a low rate of carbon and dry gas production.

In FIGURE 2 of the attached drawings, a schematic drawing of a preferred method of practicing the present invention is given.

In FIGURES 2 and 2A, oil feed having an API gravity of 5.40 is introduced through line 5 at the rate of 7960 b.p.s.d. and at a temperature of 750° F. This oil charge is comprised of 17% Kuwait reduced crude plus recycle asphalt oil in an amount to provide a recycle ratio of about 1.13:1. The reaction system consists of six reactors, A, B, C, D, E and F, respectively. At any given time, two of the reactors are on reaction cycle, consequently, in this embodiment, the oil feed passes from line 5 through line 7, containing a valve 9 in an open

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position, and thence, it enters reactor A through a header 10 depending therefrom; and it also flows through a line 11 containing a valve 13 in an open position, and thence enters reactor D through depending header 14. Each of the six reactors contain approximately 642 cubic feet of catalyst consisting of 2.7% nickel oxide, 7.3% tungsten oxide on alumina support. An average reaction temperature of about 825° F. is maintained during the reaction cycle at a total pressure of about 900 p.s.i.g. In this example, the oil feed passes upwardly through the catalyst bed, however, it should be understood that the system can operate effectively as a downflow reaction system. The quantity of oil being charged to each reactor relative to the volume of catalyst situated therein provides a volumetric space velocity of about 1.45 V₀/hr./V_c. Each reactor has a reaction cycle of four hours, therefore, the superficial catalyst to oil ratio is 0.17. Cracking of the residual oil is effected in the presence of hydrogen which is supplied through a line 16. Hydrogen containing gas enters reactor A through a line 17, which contains a valve 19 in an open position, and thence it passes through header 10 which is connected to the bottom of the reactor. In a similar manner, hydrogen is supplied to reactor D from line 16 through a second line 20 containing an open valve 22. The hydrogen rate to reactor D is substantially the same as the rate being charged to reactor A and the combined rate is 8000 s.c.f.b. At the appropriate time in the complete cycle of operation, reactors B, C, E and F will also have oil and hydrogen containing gas fed thereto in a manner similar to what has been described for reactors A and D. In the case of reactor B, the oil will pass through the line 23 containing valve 24 and hydrogen is charged thereto through line 26 containing valve 27. In the case of reactor C, the oil feed is charged through line 29 containing valve 30 and the hydrogen for the reaction cycle is supplied through line 32 containing valve 33. For reactor E, the oil is charged through line 35 containing valve 36 and the hydrogen for the reaction cycle is supplied through line 38 containing valve 39. For the end reactor F, the oil feed is charged through line 41 containing valve 42 and the hydrogen to be used with the oil feed is supplied through line 44 containing valve 45. The oil feed lines leading to reactors A, B, C, D, E, and F first pass through headers 47, 48, 49, 50, 51, and 52, respectively, prior to entering header 10 of reactor A, header 54 of reactor B, header 55 of reactor C, header 14 of reactor D, header 56 of reactor E and header 57 of reactor F. The hydrogen containing gas first passes through headers 60, 61, 62, 63, 64, and 65 of reactors A, B, C, D, E and F, respectively, prior to entering the appropriate headers thereto. By virtue of the superficial catalyst to oil ratio and the volumetric space velocity thereof during the reaction cycle, a severity factor of 0.12 is obtained.

The reaction product leaves reactor A through header 67 before passing through a line 68 containing an open valve 69. The reaction product flows from line 68 into a common header 70, and thence it passes to a system providing a preliminary separation of normally gaseous product material from the normally liquid products. Reactor D, which is also on reaction cycle, has the reaction product discharged from the header 72 into line 73 containing valve 74 in an open position, before flowing into common header 70. Similarly, when reactors B, C, E and F are on reaction cycle, the reaction product flows first through headers 76, 77, 78 and 79, respectively, and thence through lines 81, 82, 83 and 84 containing valves 86, 87, 88 and 89, respectively, before entering common header 70. The reaction product is at a temperature of about 845° F. It was indicated hereinabove, that the oil feed is preheated to a temperature of about 750° F. The temperature of the reaction product is attained by reason of the temperature at which the hydrogen containing gas is supplied to the reaction zone. In this example, the temperature of the hydrogen containing gas is 880° F.

and by virtue of the quantity at which it is supplied to the reaction zone, a resultant average reaction temperature of about 835° F. is maintained.

The reaction product flowing through common header 70 is first cooled indirectly in heat exchanger 91 to a temperature of about 610° F. before entering a second heat exchanger 92 via line 93 in which the temperature is reduced to about 450° F. The cooled reaction product leaves exchanger 92 and flows to a condenser 94 via line 95. By means of condenser 94, the temperature of the reaction product is reduced to about 110° F. The cooled reaction product flows from the condenser 94 to a flash drum 97 by means of line 98. In flash drum 97, the pressure is maintained at 880 p.s.i.a., which is essentially the same as the reaction pressure. Normally gaseous product materials are withdrawn overhead from flash drum 97 through line 100. A depending portion 102 of flash drum 97 provides for the removal of liquid water therefrom by means of a valved line 103 connected to the bottom end of this portion. The normally liquid product material at the pressure in flash drum 97 is withdrawn from the bottom thereof through a line 105, and thence it is passed to a low pressure flash drum 107. The pressure in the low pressure flash drum is 65 p.s.i.a., and the temperature is approximately 100° F. The flash material is withdrawn overhead through line 109; whereas the liquid product is removed from the bottom of flash drum 107 via line 110. The liquid product in line 110 passes through heat exchanger 91 wherein it is heated indirectly by means of the reaction product flowing from common header 70, previously described. The liquid product is heated to a temperature of about 540° F. prior to leaving heat exchanger 91 through line 111, and thence, it is passed to the product recovery system. In this example, it is contemplated charging the liquid product from line 111 to an atmospheric topping tower wherein any gasoline, furnace oil and gas oil are separated for processing in other types of systems, for example, the gas oil product is charged to a fluid catalytic cracking operation which is operated at a temperature of about 950° F., a pressure of about 10 p.s.i.g., a catalyst to oil ratio of about 8, utilizing a synthetic silica-alumina catalyst containing 85% of silica, and a weight space velocity of about 1. The total liquid product being charged to the atmospheric topping tower (not shown) has an API gravity of 16.2°, and it is produced at the rate of about 14,100 gallons per hour. The total crude oil is charged to the topping tower, hence, the asphalt product from the present operation is combined with reduced crude comprising 17% by volume thereof. By reason of the incomplete separation of gas oil from the heavy tar in the topping tower, the crude product stream comprising predominantly asphalt and reduced crude is charged to a vacuum distillation tower wherein a sharp separation is effected for the separation of tar and asphalt from gas oil, the former material constituting the feed for the reaction system under consideration.

The normally gaseous product material yielded overhead from high pressure flash drum 97 through line 100 is charged into a surge drum 115. Make-up hydrogen at the rate of 2,160,000 standard cubic feet per hour (measured at 60° F. and 760 mm.) is charged to the surge drum 115 by means of line 116. Any liquid appearing in the surge drum is discharged from the bottom end of the surge drum by means of valved line 117. The normally gaseous product material referred to hereinafter as the recycle gas, combined with the make-up hydrogen, is discharged overhead from surge drum 115 by means of line 118, and thence it is compressed to a pressure level of 965 p.s.i.g. in compressor 119. The compressed gas is discharged from compressor 119 through line 120, and this stream divides into lines 121 and 122, which in turn are connected to coils 123 and 124, respectively, in furnace 125. The heated gas is discharged from coils 123

and 124 and passed into lines 126 and 127, respectively, and these lines combine as supply line 16.

The heat contained in the reaction product is partly utilized for the production of steam. In this regard, water is supplied through a line 130 at the rate of 33,500 pounds per hour, and it is transported by means of pump 131 and line 132 into the bottom part of boiler 134. 1677 pounds per hour of water are removed from boiler 134 through a valved line 136 in order to prevent an accumulation of undesirable material in the boiler. Water is withdrawn from the bottom side of one end of the boiler 134 through a line 138, which in turn is connected to heat exchanger 92 in which the heat content of the reaction product is utilized for the production of steam. A mixture of steam and heated water is discharged from exchanger 92, and it passes into a line 139 which is connected to the top part of boiler 134. The steam manufactured by this method is discharged from the boiler via valved line 140 at the rate of 31,873 pounds per hour. A portion of the steam manufactured in this manner is utilized for purging the reaction system. Steam is charged at the rate of 2000 pounds per hour for purging through line 142. Steam purging of the reactors is effected after the reaction vessel has been depressured. This purging cycle is conducted over a 20 minute period prior to commencing downflow regeneration. When steam purging is under way each of the reactors A, B, C, D, E and F, steam is admitted into line 144 containing valve 145, line 146 containing valve 147, line 148 containing valve 149, line 150 containing valve 151, line 152 containing valve 153 and line 154 containing valve 155, respectively. The steam is vented from reactors A, B, C, D, E and F by means of a line 157 containing valve 158, line 159 containing valve 160, line 161 containing valve 162, line 163 containing valve 164, line 165 containing valve 166 and line 167 containing valve 168, respectively. Lines 157, 159, 161, 163, 165 and 167 are connected to a header 170 from which the steam used for purging is exhausted from the system.

The air supplied for the regeneration of the catalyst is admitted through line 172, and it is compressed in compressor 173 to a pressure of 110 p.s.i.g. The air is supplied at the rate of 24,600 pounds per hour. The compressed air is discharged from compressor 173 to a line 174, and it enters the top end of a surge drum 175. Any liquid which is formed during the compression stage is separated from the air stream, and it collects in surge drum 175. This condensate is removed from the surge drum 175 via line 176. The compressed air is discharged from surge drum 175 through a line 177. Cooled recycle flue gas is combined with air in line 177 by means of line 178. The flue gas is recycled at the rate of 209,000 pounds per hour, and it has a temperature of 850° F. In this particular example, the mixture of flue gas and air at 800° F. flows upwardly from line 177 into line 180. Reactors B and C are undergoing regeneration by the downflow technique. The maximum temperature of regeneration is 1150° F. Accordingly, the regeneration gas passes from line 180 into line 182 containing valve 181, and thence into header 76 of reactor B. The regeneration gas also passes through line 183 containing valve 184 and thence, into header 77 of reactor C. At appropriate intervals reactors A, D, E and F undergo downflow regeneration by the passage of regeneration gas through line 185 containing valve 186, line 187 containing valve 188, line 189 containing valve 190 and line 191 containing valve 192, respectively. In the case of reactors B and C, the flue gas resulting from downflow regeneration passes through headers 54 and 55 of these reactors, and in turn, the flue gas flows through line 195 containing valve 196 of reactor B and line 197 containing valve 198 of reactor C. The flue gas is then passed from lines 195 and 197 into a header 200. A portion of the flue gas flows into line 201 in order that it can be cooled for the purpose of recycle; whereas the remainder is vented from the system through a line 202. In the

event that reactors, A, D, E and F undergo downflow regeneration, the flue gas enters header 200 by means of line 204 containing valve 205, line 206 containing valve 207, line 208 containing valve 209 and line 210 containing valve 211, respectively.

In the case of upflow regeneration, the regeneration gas passing through lines 177 and 178 enters a main header 213. For reactors A, B, C, D, E and F, the regeneration gas being supplied through line 213 can pass through line 214 containing valve 215, line 216 containing valve 217, line 218 containing valve 219, line 220 containing valve 221, line 222 containing valve 223 and line 224 containing valve 225, respectively. The upflow regeneration is effected at a temperature of 1150° F. and a pressure of 110 p.s.i.g. The flue gas resulting from upflow regeneration is discharged from the reactors A, B, C, D, E and F through line 227 containing valve 228, line 229 containing valve 230, line 231 containing valve 232, line 233 containing valve 234, line 235 containing valve 236 and line 237 containing valve 238, respectively. The flue gas which is discharged through the lines just mentioned, enters a common header 240 which in turn is connected to another common header 200, and thence, the flue gas divides so that a portion is employed as recycle for cooling of the regeneration temperature, and the remainder is vented from the system through line 202.

Following the reaction phase of the cycle, the reactor is purged for a 1 hour period with hydrogen containing gas. In this example, the hydrogen containing gas which is supplied through common header 16, is passed upwardly through line 242 containing valve 243, and thence, it enters the bottom of reactor F via header 57. The hydrogen purge gas is discharged from reactor F through a line 84 containing valve 89, after which it flows into the header 70. Likewise, the hydrogen purge of reactors A, B, C, D and E is effected by passing hydrogen gas through line 249 containing valve 250, line 251 containing valve 252, line 253 containing valve 254, line 255 containing valve 256 and line 257 containing valve 258, respectively. Similarly, the hydrogen purge gas is discharged from reactors A, B, C, D and E through line 68 containing valve 69, line 81 containing valve 86, line 82 containing valve 87, line 73 containing valve 74 and line 83 containing valve 88, respectively. The hydrogen purge is conducted with 670,000 s.c.f.h. of gas, at a temperature of 880° F. and a pressure of 900 p.s.i.g.

Following the purge with hydrogen containing gas, the reactor is depressurized. At the appropriate time in the cycle, the gaseous material in reactor A, B, C, D, E or F is vented through line 260, 262, 264, 266, 268 or 245, respectively, and thence, it flows to a flare via line 247. Further, after upflow regeneration, the particular reactor is purged with steam, and then repressured by means of hydrogen containing gas, which is supplied through header 16. The details of the completed cycle are given in FIGURE 3, and they serve to illustrate more fully the method of operation.

The flue gas, which is recycled for the purpose of maintaining temperature control during regeneration of the reactors, flows through line 201 and enters the bottom of quench tower 280. Water supplied into the bottom part of tower 280 by means of line 281 at the rate of 21,150 pounds per hour, and it is transported to distributor 282, within the tower, by means of a pump 283 and a line 284 connected therewith. The hot flue gas is charged to the tower at a temperature and a rate sufficient to vaporize substantially all of the water which is introduced into the bottom part of tower 280. The heat requires to vaporize the water serves to cool the flue gas. Flue gas containing water vapor is discharged overhead from tower 280 by means of a line 286. The cooled flue gas is compressed by means of compressor 288, and thence, it flows into line 178 which in turn is connected to line 177 in which regeneration air is flowing to produce an oxygen containing gas at 800° F.

FIGURES 3 and 4 illustrate the processing cycles for the unit shown in FIGURES 2 and 2A.

Having thus supplied a description of our invention by means of specific examples thereof, it should be understood that no undue limitations or restrictions are to be imposed by reason thereof, but that the scope of the present invention is defined by the appended claims.

We claim:

1. A process for converting a residual oil obtained from a vacuum distillation having a gravity less than 20° A.P.I. and a carbon residue greater than about 0.6 percent by weight to a gas oil product and a heavier asphalt product which comprises contacting said residual oil with a catalyst consisting of a nickel oxide and tungsten oxide supported on alumina at a temperature of 750° to about 850° F., a pressure between about 500 and about 1500 p.s.i.g., in the presence of added hydrogen in the amount between about 2500 and about 30,000 s.c.f.b., controlling the severity factor of the reaction between about 0.09 and about 0.50 and recycling the asphalt product to the reaction zone.

2. A process which comprises converting a residual oil obtained from a vacuum distillation having a gravity less than about 13° and a carbon residue of about 5 to about 30 percent by weight to a gas oil product and an asphalt product by contacting said residual oil with a nickel-tungsten-alumina catalyst at a temperature between about 750° and about 850° F., a pressure between about 500 and about 1500 p.s.i.g., a severity factor between about 0.09 and about 0.50 in the presence of added hydrogen, said conditions being selected to provide between about 45 and about 70 percent of asphalt product and recycling the asphalt product to the reaction zone.

3. A process which comprises subjecting a crude oil to an atmospheric topping operation whereby a gas oil fraction and a reduced crude fraction including gas oil are separated therefrom, subjecting the reduced crude fraction to a distillation treatment under vacuum thus producing a second fraction of gas oil and a vacuum tar having an A.P.I. gravity less than about 20°, subjecting the vacuum tar to contact with a catalyst consisting of a nickel oxide and tungsten oxide supported on alumina at a temperature between about 675° and about 925° F., a pressure between about 500 and about 1500 p.s.i.g., a severity factor of between about 0.09 and about 0.50, in the presence of added hydrogen in the amount between about 500 and about 50,000 s.c.f.b., thus producing a mixture comprising gas oil and asphalt passing the mixture comprising gas oil and asphalt to the aforesaid atmospheric topping step for separation, separating the asphalt from the gas oil and passing the asphalt with the vacuum tar to the catalyst treating step.

4. A process which comprises subjecting a crude oil including naphtha, gas oil and reduced crude to an atmospheric topping operation whereby said fractions are produced, subjecting the naphtha to contact with a suitable reforming catalyst under reforming conditions to obtain a net production of hydrogen and a reformed liquid product, subjecting the reduced crude to a distillation treatment under vacuum to produce a second gas oil fraction and a vacuum tar, subjecting the vacuum tar having an A.P.I. gravity less than 20° and a carbon residue greater than about 0.6 percent by weight to contact with a catalyst consisting of nickel-tungsten and alumina at a temperature between about 675° and about 925° F., a pressure less than 2,000 p.s.i.g., a severity factor between about 0.09 and about 0.50 in the presence of hydrogen obtained from said reforming step in an amount between about 500 and about 50,000 s.c.f.b., thus producing a gas oil product and an asphalt product and passing said gas oil product and said asphalt product to said topping operation.

5. A process for converting a residual oil obtained from a vacuum distillation having a gravity less than 20°

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A.P.I. to a gas oil product and a heavier asphalt product which comprises contacting said residual oil with a nickel-tungsten-alumina catalyst at a temperature between about 675° and about 925° F., a pressure less than 2000 p.s.i.g., a severity factor between about 0.09 and about 0.50 in the presence of added hydrogen, and recycling the asphalt product to the reaction zone.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,043,769

July 10, 1962

Marvin F. Nathan et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 16, after "catalytic" insert -- cracking --; column 2, line 50, for "usuallly" read -- usually --; column 4, line 13, for "0.1" read -- .01 --; line 42, for "decreases" read -- decrease --; column 11, line 68, for "requires" read -- required --.

Signed and sealed this 30th day of October 1962.

(SEAL)

Attest:

ERNEST W. SWIDER
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