Inventor: John M. Brackenbury
By his Attorney: ____________________
This invention relates to the catalytic conversion of hydrocarbon oils with finely divided catalysts in fluid catalytic systems wherein the finely divided catalyst is continuously recycled through a conversion zone and through a separate regeneration zone. A particular aspect of the invention relates to the catalytic cracking of various hydrocarbon oils to produce valuable normally gaseous and normally liquid hydrocarbon products of lower molecular weight. A preferred modification of the invention relates to a combination process for the treatment of petroleum by the means of which superior Diesel fuels and fuel oils may be produced without sacrifice in the production of quality gasoline.

The nature of the invention may be most conveniently set forth by first describing a specific preferred modification thereof.

When petroleum oil is received at the refinery the gases and so-called straight run gasoline are removed leaving a partly reduced crude. The refiner is then faced with the problem of producing the maximum quantity of quality products from this partly reduced crude. One of the most valuable products desired is gasoline, and considerable effort and attention has therefore been given to various ways and means for producing the maximum quantity of gasoline of the best obtainable quality. One of the most important of the available tools at the refiner's disposal is catalytic cracking. Due to the large demand for gasoline, catalytic cracking is becoming almost universally used. Even with the best means available, however, it is not practical to convert all of this partly reduced crude to gasoline and there is left therefore a considerable volume of by-product materials of lesser value. In the past the emphasis has been largely on the production of the maximum quantities of gasoline of the best quality and the by-products formed or left have largely determined the quantity and quality of secondary products such as fuel oil, kerosene, stove oil, asphalt, coke, etc., produced.

The various fractions of the partly reduced crude are considerably different in composition and character and some are much more amenable to catalytic cracking than others. In general the feeds preferred and used for catalytic cracking units are those fractions taken from the middle of the partly reduced crude. These fractions are of the nature of light gas oil or stove oil. The lower boiling components of the nature of heavy gasoline, naphtha and kerosene are more refractory and are generally used in secondary products or treated by thermal methods, although in a few cases they are catalytically cracked along with the light gas oil. Also, the bottom fraction, or reduced crude cannot be completely vaporized and is not suited for vapor phase catalytic cracking. In practice the gas oil and stove oil are removed as completely as possible under ordinary fractionation conditions to leave a reduced crude which is suitable for use as fuel oil. In a few cases this reduced crude has been partly vaporized in a so-called contact vaporizer and the vapors cracked along with the gas oil. This is not usually economical however, since no fuel oil is produced, and a large amount of coke must be burned in the contact vaporizers. The common present practice is to subject this reduced crude to thermal cracking to produce cracked gasoline and a cracked fuel oil residue. The present war time operations using catalytic cracking are described in National Petroleum News, 36, R99, February 2, 1944. When handling the petroleum by these methods excellent yields of quality gasoline are generally produced, but only at the expense of the quantity and quality of various other petroleum products such as Diesel oil and fuel oil. A primary object of the particular modification of the invention about to be described is to provide a method whereby the petroleum may be utilized to better advantage by producing quality gasoline from the more refractory fractions of the partly reduced crude without sacrificing yield or quality of secondary products.

To the accomplishment of this and related objects the partly reduced crude is separated by fractional distillation into a naphtha (or heavy gasoline) fraction, a heavy reflux condensate including kerosene, gas oil and stove oil, and a reduced crude. The reduced crude is not however thermally cracked as is the general practice, but is subjected to a flash distillation under reduced pressure to produce a heavy flashed condensate and a heavy tar residue. The naphtha fraction and the heavy flashed condensate are then simultaneously cracked catalytically. The naphtha and the heavy flashed condensate are both relatively refractory materials and are individually less suited for catalytic cracking than the intermediate gas oil and stove oil fractions. It has been found, however, that these two refractory stocks may advantageously be catalytically cracked together under suitable conditions. By producing the major part of the cracked gasoline from these materials excellent yields of quality gasoline may be produced without sacrifice of
quality Diesel fuel production and while affording a superior fuel oil. However, because of the totally different characters of these two feed stocks and the greater refractivity of the naphtha fractions the maximum efficient production of gasoline is not obtained when cracking these mixed feeds simultaneously under the said cracking conditions. The cracking of these two stocks simultaneously under optimum conditions is effected, according to the process of the present invention, as hereinafter described.

The process will be described in the following in connection with Figures I and II of the accompanying drawing in which this specific embodiment of the invention is set forth for purposes of illustration. In the accompanying drawing, Figure I is a simplified flow diagram wherein there is shown by means of diagrammatic figures, the schematic arrangement of apparatus arranged for operation according to this particular embodiment of the invention. Figure II is a diagrammatic illustration of a suitable reactor in section.

The charging stock is a crude petroleum or one from which the gasoline has been substantially removed. If a crude petroleum containing gasoline is used, the gasoline is preferably removed to leave a partly reduced crude having an initial boiling point of at least 350°F. The feed is then separated by distillation into a naphtha fraction, a heavy reflux condensate and a reduced crude. The cut point between the naphthas and the reflux condensate may vary considerably, but is preferably between about 400°F and 500°F. This separation may be effected in conventional equipment in a number of ways. In the modification illustrated in Figure I of the attached drawing a crude petroleum enters via line I and is charged by pump 2 to a stripping column 3 wherein gasoline and naphtha are separated.

The gasoline and naphthas are removed overhead via line 4. Part of the condensate is returned as reflux and the remainder is passed to a fractionation column 5 wherein gasoline is separated from the naphtha. The gasoline passes overhead via line 6. The naphtha fraction having a boiling range of, for instance, 325 to 450°F, is removed via line 7a. The bottom product from column 3 is passed through a suitable heater and then via line 8 to a fractionating column 5. In column 5 substantially all of the hydrocarbon that can be removed at atmospheric pressure without substantial cracking are removed. The various products may be removed in a single stream or may be segregated into various fractions as desired. Thus, for example, in the annexed drawing, a heavy naphtha or kerosene fraction is removed via line 10; a light gas oil fraction suitable for use as Diesel fuel is taken off via line 11; and a heavy gas oil fraction suitable for use as Diesel fuel or for stove oil is taken off via line 12. The bottom product is a reduced crude suitable for use as fuel oil.

The reduced crude is passed through heating coils in a suitable heater and then via line 13 and pressure control valve 18a to a vacuum flash column 14 wherein it is vacuum flashed under conditions chosen to remove between about 40% and about 75% of a heavy flashed condensate having a molecular weight between about 270 and about 350. One set of typical conditions is, for example, a temperature of about 700 to 750°F, and 100 mm, absolute pressure. Steam may be injected via line 19 to aid in decreasing the residence time and prevent cracking. The flashing operation does not involve any appreciable amount of cracking. This is indicated by the average molecular weight of the flashed condensate. Thus, the average molecular weight of the flashed condensate when taking 45% overhead is about 230, and the average molecular weight when taking 70% overhead is about 345. In general a condensate having an average molecular weight in this range is indicated. This flashed condensate, it is seen, represents the heaviest portion of the petroleum that can be vaporized with available equipment without substantial cracking. It is difficult to vaporize, and invariably contains appreciable amounts of nitrogen compounds and other impurities.

The material removed from the bottom of the flash column 14 is a heavy viscous residue. This material is totally unsuited for fuel oil, but produces a superior fuel oil when combined with aromatic reflux condensate as hereinafter described.

In a preferred modification of the process of the invention the flashing operation is carried out under somewhat more severe conditions to effect a slight controlled amount of cracking. The amount of cracking is adjusted to give between about 50% and 75% of a condensate having an average molecular weight between about 280 and 300. This may be and is preferably effected with the formation of not more than 1% gas and not more than 1% of gasoline, i.e., normally liquid products boiling up to 400°F. This operation is effected at temperatures below about 840°F, for instance temperatures between about 780°F and 850°F. The conditions of pressure and residence time to give this result cannot be stated with any degree of definiteness due to the interrelation of these factors and the differences due to the particular petroleum source and apparatus effects. However, these conditions are adjusted in the known manner and may be readily arrived at in any particular case. The distillate obtained under such conditions is hereinafter referred to as flash cracked condensate.

The naphtha fraction separated in column 3 is fed by line 7 to a suitable fluidized catalyst cracking reactor 17. This feed picks up and carries to the reactor a quantity of hot freshly regenerated catalyst from the outlet of the fluidized catalyst regenerator 20. In some cases the heat supplied by the hot freshly regenerated catalyst may be sufficient to vaporize the naphtha and heat it to the desired cracking temperature. The naphtha is however quite refractory and for best results is cracked at temperatures higher than those generally applied for the catalytic cracking of gas oils and similar stocks. It is therefore generally necessary to preheat the naphtha feed prior to contacting it with the catalyst. Thus, the naphtha feed may be passed through the coils of a suitable heater 21. The naphtha containing suspended freshly regenerated catalyst is introduced into the fluidized catalyst reactor at or near the bottom in the conventional manner. The flashed condensate or flash cracked condensate is passed through the coils of a suitable heater 21 and then the fluidized catalyst reactor 17. The preheated flashed condensate or flash cracked condensate is, however, introduced into the reactor at a point well above the point of introduction of the naphtha and fresh catalyst. Partially spent catalyst is continuously withdrawn from the reactor by standpipes 24 and 25. This material is picked
up and carried to the regenerator 28 by a stream of regeneration gas entering via line 28. Spent regeneration gas is withdrawn from the system by line 27. The mixture of cracked and uncracked products is passed, as a vapor substantially free of catalyst, by line 29 to a fractionator 29 wherein the gas and catalyst are separated from the heavier cracked and uncracked material. The gasoline and gas are removed overhead via line 30, condenser 31 and separator 32.

The gas which is separated and removed may be sent to a gas controller and the gasoline may be returned to the column 29 for reflux. The remainder is withdrawn via line 33.

A heavy aromatic condensate is removed via line 35, cooler 36, surge tank 37 and pump 38 and a heavy residue is removed via line 34. This heavy residue contains a small amount of catalyst and may be advantageously recycled back to the cracking reactor via line 7. The condensate consists largely of highly refractory aromatic hydrocarbons produced in the cracking zone. This material is passed via line 39 to a tank 40 wherein it is blended with the hot vacuum flashed residue, coming from the vacuum flash column 14 via line 42. In view of the highly aromatic nature of the condensate it blends well with the very heavy vacuum flashed residue to produce a stable and superior fuel oil. Also due to its extreme refractoriness and low ratio of hydrogen to carbon it is a very poor cracking stock and also a very poor Diesel fuel. On the other hand, this relatively small quantity of material is capable of converting a relatively large volume of heavy vacuum flashed residue into a superior fuel oil. Thus, in general it requires only about 50 parts of the aromatic condensate to convert 100 parts of the heavy flashed residue into a superior 100 second (Saybolt-Furol—122°F) fuel oil. When blended 1:1 the heavy flashed residue is converted to a stable 25 second (Saybolt-Furol—122°F) fuel oil meeting the Navy special grade specifications.

Figure 11 is a somewhat more detailed illustration of the fluid catalytic reactor 17. The naphtha stock is fed into the reactor at the bottom via line 1 and the distributing manifold 45. Partially spent catalyst is withdrawn from the bottom via standpipes 24 and 25. The rates of addition and withdrawal of catalyst are so adjusted as to maintain in the reactor a substantial bed of the catalyst as illustrated. The rate of flow of vapors is so controlled that the catalyst is maintained in a pseudo liquid or fluidized state. The flashed condensate or flash cracked condensate entering via line 23 is injected into the fluidized bed of catalyst by means of a distributing manifold 46. The reactor at the height of the manifold 46 is preferably increased in diameter, as shown, so as to accommodate the increased volume of vapors contacting the upper half of the fluidized bed of catalyst. The space in the reactor above the catalyst bed is provided to allow separation of suspended particles of the catalyst from the vapors leaving the catalyst bed. A number of cyclone separators 47 may advantageously be provided in the upper disengaging space to afford a more complete removal of suspended catalyst particles.

The described embodiment of the invention may be carried out using any of the solid refractory metal oxide or clay-type cracking catalysts. Suitable catalysts are, for example, the synthetic clay-type metal oxide composition catalysts such as silica-alumina, silica-alumina-zirconia, silica-magnesia, silica-alumina-aluminum fluoride, alumina-boric oxide, silica-alumina-boric oxide and silica gel promoted with one or more metal oxides adsorbed thereon. Also the natural or treated clay catalysts such as material known as Filtril may be used. These materials may furthermore comprise minor amounts of promoting compounds such as the oxides or sulfides of molybdenum, chromium, tungsten, vanadium and the like. These various cracking catalysts are not necessarily equivalent and by the proper choice of catalyst it is possible to obtain almost any desired balance of such factors as the octane number of the gaseous butylene products, etc. A balance of products particularly suitable for present refinery operation is obtained with the following proprietary cracking catalysts: boric oxide on peptized alumina, silica-alumina composite cracking catalysts, and silica-magnesia composite cracking catalysts.

As pointed out above the feed stocks cracked according to the described modification of the invention are relatively refractory, i.e., under normal cracking conditions such as used for cracking a clean naphthenic gas oil, the production of gasoline would be quite low. The refractory nature of the two feeds are however different in nature. The naphtha feed is inherently refractory due to the relatively low molecular weight of the hydrocarbon constituents. The flashed condensate and flash cracked condensate on the other hand are composed of hydrocarbons of high molecular weight and the refractivity appears to be largely due to the presence of minor amounts of poisons such as sodium bases, etc., which are invariably present. This material is therefore actually less refractory than the naphtha and is preferably cracked under different conditions. According to the process of the invention such less refractory materials are cracked under the optimum temperature conditions for the combined feeds but at a higher space velocity. This is accomplished by supplying all or the major part of the hot, fresh catalyst with the more refractory naphtha and introducing the flashed condensate or flash cracked condensate at an intermediate point in the reaction zone as described. By control of the rates of oil flow and/or by control of the depth of the bed of fluidized catalyst maintained in the reaction zone a considerable variation of the space velocities for the individual feeds may be obtained. Also, the naphtha fraction may be cracked at a weight hourly space velocity of, for example, 0.4 to 2 pounds of oil per pound of catalyst per hour and the flashed condensate or flash cracked condensate may be simultaneously cracked at a higher space velocity of, for example, 1 to 4 pounds of oil per pound of catalyst per hour.

The remaining cracking conditions may vary individually over a considerable range depending upon the characters of the individual feed stocks, the space velocities employed, etc. These are adjusted in the known manner to give the desired results for the particular operation at hand. The approximate ranges of the individual conditions for general operation are as follows:

- Temperature: —°F—325—1100
- Pressure: —ps. i. g. —10—100
- Catalyst/oil weight ratio: 10:1—30:1
- Steam: —per cent of oil: 0—25

The relative amounts of the light naphtha and flashed condensate available from a given petroleum depends upon the particular petro
the depth of flashing, and may vary considerably. In some cases the available refractory naphtha, of say 320-450° F. boiling range, may be more than enough to form a satisfactory blend with the flashed condensate. In this case the boiling range of the naphtha may be reduced to say 320-405° F., or part of the naphtha may be used for other purposes. Also, certain other heavy residues may be added to the reduced crude to increase the amount of flashed condensate. In general ratios of flashed condensate to naphtha of from about 1:1 to about 10:1 are preferred.

It is to be noted that according to the prevalent belief in the art, the described mixture of flashed condensate and light naphtha would not be considered a desirable feed for catalytic cracking. The light naphtha, it will be noted, contains appreciable quantities, and may even consist essentially, of hydrocarbons which can properly be considered as gasoline components. In fact, the light naphtha could in many cases also be called a heavy straight run gasoline. When cracking gas oil, stove oil, and similar intermediate distillates, it is known that the presence of gasoline constituents in the feed is quite harmful. The present belief to the art is that such gasoline components should be absent from all catalytic cracking stocks. In the present process this harmful effect of gasoline components is not noticed, and, on the contrary, the light naphtha in the present process is distinctly beneficial in certain respects. Thus, the naphtha fraction is quite refractory and is preferably cracked at high cracking temperatures. When this material is cracked alone it is difficult to maintain the optimum high cracking temperatures. On the other hand the flash condensates and flashed cracked condensates invariably contain considerable amounts of impurities such as nitrogen compounds. If these materials are cracked alone, in large amounts of coke are formed and the conversions are low, apparently due to the poisoning effect of these impurities. When, however, the naphtha fraction and the flashed condensate or flash cracked condensate are cracked together these disadvantages tend to cancel each other to a certain extent. Thus, the naphtha tends to reduce the concentration of nitrogen bases, etc., and the flashed condensate tends to increase the coke production over that of the naphtha alone, thus providing more heat in the regeneration zone. This heat is largely conveyed to the reaction zone by the hot regenerated catalyst. Furthermore, the flashed condensates and flash cracked condensates are quite heavy and difficult to maintain entirely in the vapor phase without the use of a large amount of steam. The relatively light naphtha acts as a diluent and is very beneficial in this respect also.

The above described modification of the present process, it will be seen, allows the production of considerable yields of excellent Diesel fuel from the virgin naphtha without impairing the quality or quality of gasoline produced. The gasoline produced and the flashed condensate or flash cracked condensate while taking advantage of some gasoline production from the refractory naphtha and at the same time producing therefrom a refractory aromatic condensate which is compatible with flashed residue and flash cracked residue may be used to convert these residues to superior fuel oils. Thus, the process allows the petroleum to be utilized to better advantage without sacrificing yield or quality of secondary products.

I claim as my invention:
1. In the production of useful products including gasoline and fuel oil from petroleum, the process comprising separating the petroleum by distillation into a naphtha fraction boiling between about 320° F. and 450° F., a heavy reflux condensate and a reduced crude, subjecting the reduced crude to a flash distillation under reduced pressure and under mild cracking conditions to produce a heavy residue and between 50% and 75% of a heavy flash cracked condensate having a molecular weight between about 280 and 300 with the formation of less than 1% gas and less than 1% gasoline, mixing said naphtha fraction with a finely divided cracking catalyst and conveying the mixture to the bottom of a cracking zone containing fluidized cracking catalyst, introducing at an intermediate point in said cracking zone said heavy flash cracked condensate thereby to simultaneously crack said naphtha at a relatively low space velocity and said heavy flash cracked condensate at a relatively high space velocity separating the cracked product into a gasoline fraction and a heavy aromatic condensate, and combining said heavy aromatic condensate with said heavy residue to produce fuel oil.

2. In the production of useful products including gasoline and fuel oil from petroleum the process comprising separating the petroleum by distillation into a naphtha fraction boiling between about 320° F. and 450° F., a heavy reflux condensate, and a reduced crude, subjecting the reduced crude to a flash distillation under reduced pressure and under mild cracking conditions to produce a heavy residue and between 50% and 75% of a flash cracked condensate having a molecular weight between about 280 and 300 with the formation of less than 1% gas and less than 1% gasoline, passing said naphtha through a catalytic cracking zone in contact with a fluidized finely divided cracking catalyst, introducing into the partially cracked naphtha in said cracking zone said heavy flash cracked condensate, thereby to simultaneously crack said heavy flash cracked condensate in the presence of partly cracked naphtha, separating the cracked products into a gasoline fraction and a fraction of nitrogen bases, etc., and combining said heavy aromatic condensate with said heavy flashed residue to produce fuel oil.

3. In the production of useful products including gasoline and fuel oil from petroleum, the process comprising separating the petroleum by distillation into a naphtha fraction boiling between about 320° F. and 450° F., a heavy reflux condensate, and a reduced crude, subjecting the reduced crude to a flash distillation under reduced pressure to produce a heavy residue and between 40% and 75% of a heavy flashed condensate having a molecular weight between about 270 and 350, mixing said naphtha fraction with a finely divided cracking catalyst and conveying the mixture to the bottom of a cracking zone containing fluidized cracking catalyst, introducing at an intermediate point in said cracking zone said heavy flashed condensate, thereby to simultaneously crack said naphtha at a relatively low space velocity and said heavy flashed condensate at a relatively high space velocity, separating the cracked product into a gasoline fraction and a heavy aromatic condensate and combining said heavy aromatic condensate with said heavy residue to produce fuel oil.

4. In the production of useful products including gasoline and fuel oil from petroleum, the
process comprising separating the petroleum by distillation into a naphtha fraction boiling between 300° F. and 500° F., a heavy reflux condensate, and a reduced crude, subjecting the reduced crude to a flash distillation under reduced pressure to produce a heavy residue and between about 40% and 75% of a heavy flashed condensate having a molecular weight between about 270 and 350, passing said naphtha through a catalytic cracking zone in contact with a fluidized finely divided cracking catalyst, introducing into the partly cracked naphtha in said cracking zone said heavy flashed condensate, thereby to simultaneously catalytically crack said heavy flashed condensate in the presence of partly cracked naphtha, separating the cracked products into a gasoline fraction and a heavier aromatic condensate and combining said heavier aromatic condensate with said heavy flashed residue to produce fuel oil.

5. In the production of useful products including gasoline and fuel oil from petroleum, the process comprising separating the petroleum by distillation into a naphtha fraction boiling between about 320° F. and 450° F., a heavy reflux condensate, and a reduced crude, subjecting the reduced crude to a flash distillation under reduced pressure to produce a heavy flashed condensate and a heavy residue, mixing said naphtha fraction with a finely divided cracking catalyst and conveying the mixture to the bottom of a cracking zone containing fluidized cracking catalyst, introducing at an intermediate point in said cracking zone said heavy flashed condensate, thereby to simultaneously crack said naphtha at a relatively low space velocity and said heavy flashed condensate at a relatively high space velocity, separating the cracked product into a gasoline fraction and a heavy aromatic condensate and combining said heavier aromatic condensate with said heavier residue to produce fuel oil.

6. In the production of useful products including gasoline and fuel oil from petroleum, the process comprising separating the petroleum by distillation into a naphtha fraction boiling between 300° F. and 500° F., a heavy reflux condensate, and a reduced crude, subjecting the reduced crude to a flash distillation under reduced pressure to produce a heavy flashed condensate and a heavy flashed residue, passing said naphtha through a catalytic cracking zone in contact with a fluidized finely divided cracking catalyst, introducing into the partly cracked naphtha in said cracking zone said heavy flashed condensate, thereby to simultaneously catalytically crack said heavy flashed condensate in the presence of partly cracked naphtha, separating the cracked products into a gasoline fraction and a heavier aromatic condensate, and combining said heavier aromatic condensate with said heavy flashed residue to produce fuel oil.

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