Sept. 25, 1945. W. A. BAILEY, JR 2,385,326

CATALYTIC TREATMENT OF HYDROCARBON OILS

Filed Sept. 19, 1944 3 Sheets-Sheet 1

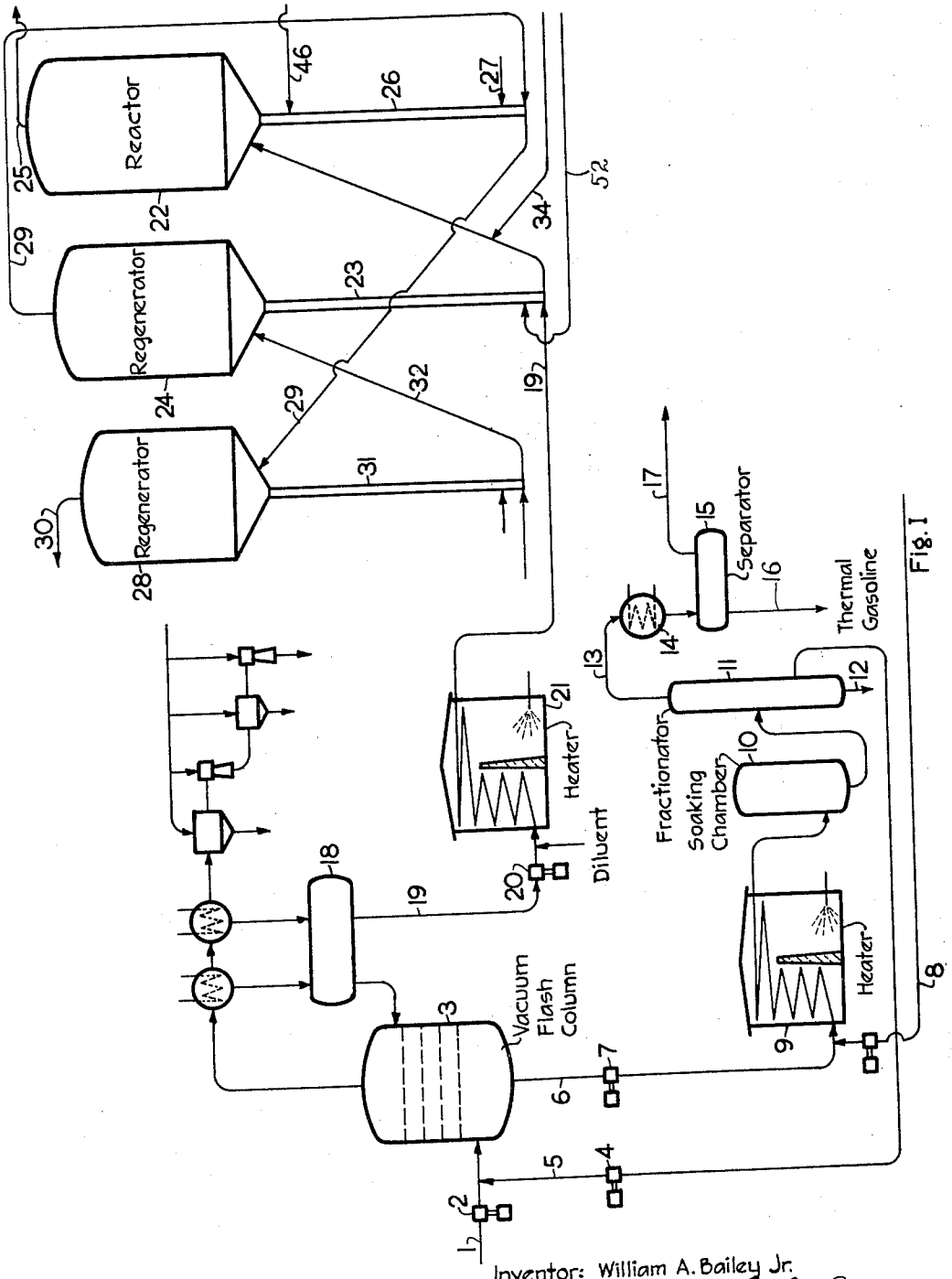


Fig. 1

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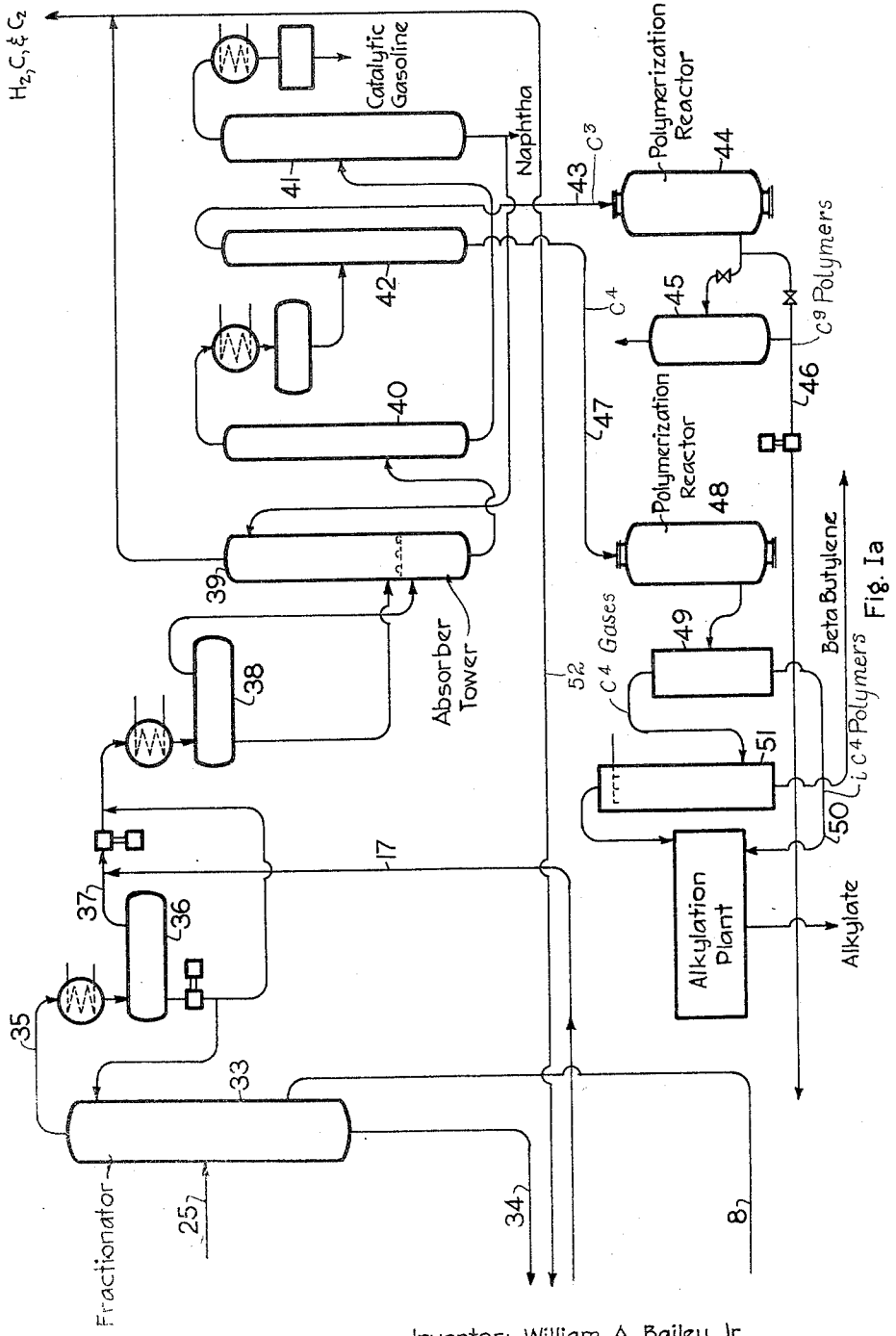


Fig. Ia

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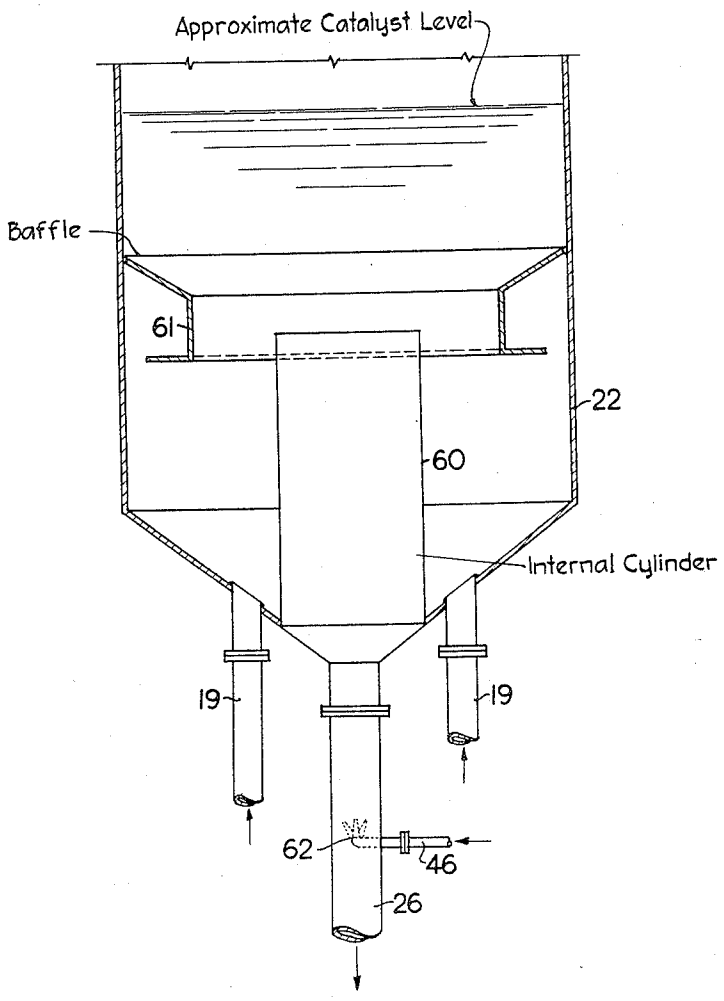


Fig. II

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UNITED STATES PATENT OFFICE

2,385,326

CATALYTIC TREATMENT OF HYDROCARBON OILS

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Application September 19, 1944, Serial No. 554,817

7 Claims. (Cl. 196—52)

The present invention relates to the continuous catalytic cracking of hydrocarbon oils to produce valuable normally gaseous and normally liquid hydrocarbons of lower molecular weight. More particularly the invention relates to a process for the continuous catalytic cracking of certain hydrocarbon oils under special conditions to produce large yields of beta butylene and first quality C_8 alkylate with small ultimate yields of propylene and propylene alkylate.

The main advantage of catalytic cracking and the primary reason why it has been accepted by the industry is that when combined with thermal cracking it affords a means of producing more hydrocarbons of the gasoline boiling range than thermal cracking or catalytic cracking alone. A secondary advantage of catalytic cracking over thermal cracking has been considered to be the fact that catalytic cracking generally produces a cracked gasoline of better quality. Consequently catalytic cracking has invariably been used in the past in combination with thermal cracking and primarily to produce gasoline. The conditions etc. have been chosen primarily with the production of gasoline, and particularly aviation base stock, in mind.

In catalytic cracking to produce gasoline it has been previously noted that the gases produced generally contain more propylene, butylenes, and isobutane, and less methane, ethane, ethylene, and normal butane than those obtained in thermal cracking. In general the olefinic gases, other than ethylene, produced in both cracking operations are alkylated with isobutane to produce additional quantities of valuable gasoline. This, however, generally requires the operation of a separate process for the isomerization of normal butane to isobutane in order to supply sufficient isobutane to balance the olefin production. Lack of a suitable source of isobutane has seriously curtailed the production capacity for alkylate in many refineries. Under such circumstances it would be logical to alkylate only the C_4 olefins since these give a much better quality alkylate than the propylene. However, there is a great demand for butylenes, and particularly beta butylene, for the production of butadiene and for other chemical uses. It has therefore been necessary to alkylate the propylene.

An object of the present invention is to provide a method for the cracking of hydrocarbon oils which affords exceptionally large yields of valuable gaseous hydrocarbons, particularly beta butylene and isobutane. Another object of the invention is to provide a process which gives low ultimate yields of propylene. Still another object of the invention is to provide a process in which the production of isobutane substantially balances the production of isobutylene and thus allows a maximum production of first quality C_8 alkylate per barrel of feed.

There are at present two systems available for the continuous catalytic cracking of hydrocarbon oils. The first of these is the moving bed systems typified by the Thermofor catalytic cracking process. In this process the catalyst in the form of pellets or particles is slowly passed through a catalytic cracking zone and continuously recycled by mechanical means through a similar catalyst regeneration zone. The second is the fluid catalyst systems typified by the Fluid catalyst cracking process. In this system the catalyst in the form of a finely divided powder (usually passing a 100 mesh screen) is recirculated through suitable cracking and regeneration zones by means of gas or vapor streams. The catalyst in the cracking zone is maintained in a pseudo liquid or fluidized state. The process of the present invention relates in particular to a catalytic cracking process making use of this latter type of system.

Although various stocks may be catalytically cracked, the continuous catalytic cracking processes are most advantageously applied for the cracking of relatively clean stocks, such, in particular, as gas oil. In the cracking operation coke is deposited on the catalyst and this coke is burned from the catalyst in a separate regeneration zone. Since the burning of this coke is the most costly and difficult operation of the process and since the coke burning capacity is, in general, the factor limiting production rate, every effort is made to maintain the rate of coke production at a minimum. For these reasons various cracking feeds which would tend to give large amounts of coke are cracked in the auxiliary thermal unit. A further object of the present invention is to provide a method for the catalytic cracking of hydrocarbon oils with a low production of coke, thereby allowing many refractory, dirty and contaminated stocks to be catalytically cracked without exceeding the coke burning capacity of the regenerator. The above and other related objects of the invention are realized in the process hereinafter described.

The process of the invention in its broader aspect comprises catalytically cracking a hydrocarbon oil in a fluid catalyst system under special conditions chosen to produce large amounts of

gaseous products, separating C_4 hydrocarbons from the product gases, subjecting a fraction of the product gases to a selective polymerization treatment under conditions to convert propylene predominantly to C_9 polymers, separating the polymers so formed and catalytically cracking them in admixture with the initial feed stock, but at a much higher space velocity, thereby to produce additional quantities of butylene and isobutane. In preferred embodiments of the invention the catalytic cracking process is used in conjunction with thermal cracking and the gaseous products from the thermal cracking treatment are similarly treated; the finely divided catalyst is regenerated in a special manner to allow much higher temperatures to be employed in the catalytic cracking step and to thereby afford optimum conditions for the production of large quantities of gaseous products; isobutylene is selectively polymerized and separated from the C_4 fraction; beta butylene is separated as a product of the process; isobutylene polymer and the residual C_4 fraction consisting largely of isobutane are then available for alkylation. In order to facilitate the above mentioned treatments of the gaseous products of the cracking step, residual product gases are injected into the fluid catalyst regenerator standpipe.

The process of the invention will be described more particularly in connection with the attached drawings. Figures I and I*a* taken together show by way of illustration a flow diagram of a typical operation. Figure I is an elevation, partly in section of the lower part of a suitable fluid catalyst reactor of the bottom-draw-off type.

The process of the invention is applicable for the cracking of a wide variety of hydrocarbon oils. Thus, various oils such as naphthas, kerosenes, gas oils, stove oils or reduced crude petroleums may be cracked in the catalytic cracking system. However, the process of the invention is most advantageous when the catalytic cracking system is applied for the cracking of feeds which normally tend to produce large quantities of gaseous products. Also it is most advantageous when the catalytic cracking step is operated under conditions chosen to produce large yields of desired olefins rather than under the usual conditions adapted to produce maximum yields of quality gasoline. Thus, the present process is ideally suited for the catalytic cracking of heavy refractory stocks which are, relatively speaking, unsuited for the production of quality gasoline. Such a material is the heavy condensate obtained by vacuum flashing straight run residues. The thermal cracking system, if it is used, may be used to crack any of these materials or such heavy materials as tars, heavy residues, etc. It is, however, usually used to crack the refractory higher boiling products of the catalytic system. In the system illustrated the thermal cracking unit is used to crack a mixture of heavy tar obtained from such a vacuum flashing operation and catalytic gas oil.

The operation illustrated in the flow diagram then is a typical operation using as a preferred feed material a reduced crude petroleum and is not to be construed as limiting the invention to the treatment of such a material.

Referring now to the flow diagram, Figure I, the reduced crude, entering on the left via line **1**, is charged by pump **2** to a vacuum flash column **3**. A thermally cracked gas oil fraction may also be charged simultaneously via pump **4** and line **5**. The vacuum flash column is operated at a pressure usually between about 100 mm. and 200 mm. absolute and at a temperature between about 700° F. and 820° F. to remove as an overhead product between about 40% and about 75% of the reduced crude feed. Although the flashing operation does not depend upon any cracking of the charged oil a small amount of cracking may take place. In general the overhead product from the flashing operation has a molecular weight between about 280 and 345. This overhead product, or flashed condensate, invariably contains considerable nitrogen and sulfur compounds and other impurities and in catalytic cracking normally gives a high coke production and relatively poor yields of relatively poor quality gasoline.

The bottom product from the vacuum flash column is a heavy tar residue. This material is withdrawn via line **6** and pump **7**, mixed with catalytic gas oil entering via line **8**, and subjected to a thermal cracking treatment. Thus, the mixture is passed through cracking coils in heater **9** to a soaking chamber **10**. The products pass to a fractionator **11**. Residue is withdrawn from the bottom of fractionator **11** by line **12**. A thermally cracked gas oil fraction is withdrawn via line **5** and recycled to the vacuum flash column **3**. Gasoline and gas are withdrawn overhead via line **13** and condenser **14** to a separator **15**. Gasoline is withdrawn via line **16** and gaseous products are withdrawn via line **17**. These gaseous products are rich in propylene and are handled along with the gases from the catalytic cracking operation as will hereinafter be described.

The heavy flashed condensate from the vacuum flashing operation is withdrawn from condensate drum **18** via line **19** and pump **20**. This material is preheated in a suitable heater **21** and charged to the fluid catalyst catalytic cracking reactor **22**. Thus the oil charge in line **19** picks up a quantity of freshly regenerated finely divided cracking catalyst from the standpipe **23** of the secondary fluid catalyst regenerator **24** and carries it to the fluid catalyst cracking reactor. The mixture enters the reactor near the bottom as indicated. The hydrocarbon vapors pass up through a bed of the fluidized finely divided catalyst and pass out of the reactor at the top via line **25**.

Partially spent catalyst is continuously withdrawn from the reactor **22** by standpipe **26**. A small amount of a gas or vapor is introduced near the bottom of the standpipe via line **27** to maintain the catalyst in the standpipe in a free-flowing condition. The partially spent catalyst is preferably regenerated in a special manner which allows it to be heated to exceptionally high temperatures and thereby allows the cracking to be carried out at higher temperatures. Thus, the partially spent catalyst withdrawn by standpipe **26** is picked up and carried by a stream of regeneration gas of low oxygen concentration to a primary or low temperature regenerator **28** via line **29**. In the low temperature regeneration the more easily combustible deposits leading to the formation of water of combustion are burnt. The spent regeneration gas containing water of combustion is withdrawn via line **30**. The temperature in the primary regenerator may be maintained below about 1100° F., for instance about 1000° F. The partially regenerated catalyst from the primary regenerator **28** is withdrawn via standpipe **31**. This catalyst is picked

up by a stream of air and carried via line 32 to the secondary or high temperature regenerator 24. The temperature in regenerator 24 may be maintained above 1100° F., for instance 1200° F.–1350° F. The gases from the secondary regenerator are advantageously used as regeneration gas for the primary regenerator.

The catalytic cracking step is preferably carried out at a temperature of about 1000° F. or above. This is made possible by the sensible heat of the hot freshly regenerated catalyst fed to the reactor with the incoming oil feed. The use of such high temperatures is highly advantageous in two respects. The use of such temperatures affords higher yields of the desired gaseous products. Also, the use of such temperatures leads to the formation of a lesser amount of coke for a given depth of cracking. The other conditions in the cracking reactor may be varied considerably but are preferably sufficiently severe to convert at least 10% of the charged oil into normally gaseous products. Thus the cracking may be carried out at atmospheric pressure or moderate superatmospheric pressures up to about 10 atmospheres, and any of the common cracking catalysts used in fluid catalyst cracking systems may be used. Very suitable catalysts are for example the various synthetic composite catalysts of silica-alumina, or silica-alumina-zirconia, or silica-magnesia, or alumina-silica-boria. Particularly suitable catalysts are however those containing a major amount of alumina promoted with minor amounts of silica and boria, and the silica-magnesia catalysts since these catalysts give exceptionally large yields of the desired gaseous olefins. These catalysts may also be improved for the present operation by the incorporation of minor amounts of dehydrogenating compounds such as chromium oxide, molybdenum oxide, vanadium oxide, titanium oxide, cobalt oxide, manganese oxide, or cobalt molybdate. These materials may be incorporated directly into the cracking catalysts, but are preferably mixed with the finely divided cracking catalyst as discrete particles.

The production of desired gaseous olefins may also be increased by dilution of the feed with an inert gas. In general steam is the preferred diluent, but other inert gases such as methane, ethane, carbon dioxide, and ammonia, can be used. If steam is used, for example, a mole ratio of steam to hydrocarbon of at least 2:1 may be advantageously employed.

The product from the cracking reactor 22 passes via line 25 to a fractionator 33, Figure Ia. A small bottom fraction containing a small amount of catalyst carried over with the product vapors is withdrawn from the bottom and is preferably recycled to the reactor via line 34 and 19. A catalytic gas oil fraction is withdrawn via line 8. This fraction may advantageously be cycled to the thermal cracking unit as shown. The overhead fraction withdrawn via line 35 is cooled and passed to a separator 36. The gaseous products are withdrawn via line 37. This gaseous fraction, preferably in admixture with the gaseous products from the thermal operation, is compressed, mixed with the liquid product, cooled and again separated in high pressure separator 38. The products from the high pressure separator are passed to a conventional absorber tower 39 using naphtha as the absorber oil. The gaseous products withdrawn from the absorber consists essentially of a H_2, C and C_2 fraction. This fraction may be withdrawn from the system as a product of the process. A portion of this fraction may, however, be advantageously recycled via line 52 to the standpipe 23 of the high temperature regenerator 24. The amount recycled is adjusted to displace the air in the regenerated catalyst and consequently this recycled material is recycled and not burned in the regenerator. The use of this recycle decreases the losses and contamination of the H_2, C_1 and C_2 fraction with large amounts of nitrogen and carbon dioxide. The bottom fraction from the absorber is passed to a stripper 40. The bottoms from the stripper pass to a fractionator 41 wherein the catalytic gasoline is separated from the naphtha which is partly withdrawn and partly recycled to the absorber. The top fraction from the stripper 40 passes to a fractionator 42 wherein it is separated into a C_3 fraction and a C_4 fraction. These two fractions are separately subjected to selective polymerization treatments. Thus the C_3 fraction withdrawn via line 43 is passed to a polymerization reactor 44 operated in a known manner to selectively polymerize propylene essentially to C_9 polymers. The product may, if desired, be separated in a column 45 from propane and any other unreacted materials.

The C_9 polymer removed via line 46 may be catalytically cracked to give large yields of butylenes and isobutane. The severe conditions necessary for the catalytic cracking of the relatively refractory flashed condensate are, however, much too severe for the catalytic cracking of such polymers and would convert them largely into undesired products if the C_9 polymers were simply recycled with the flashed condensate. This difficulty is avoided, however, by cracking the C_9 polymers simultaneously with the flashed condensate, but at a higher space velocity. This condition can be obtained by injecting the C_9 polymers into the fluid catalyst reactor in such a way that they contact only a portion of the catalyst therein, and preferably a partially spent portion. This may be accomplished by injecting the C_9 polymer into the standpipe 1 of a fluid catalyst reactor such as illustrated diagrammatically in Figure II of the attached drawings.

Referring to Figure II it will be seen that the fluid catalyst reactor is more or less of the conventional type. The reactor consists essentially of a cylindrical shell (which in a typical cracking plant is about 25 feet in diameter) with conical ends. The bottom of the lower cone connects with a vertical standpipe or catastat (which in a typical case is about 5 feet in diameter). In the lower cone, surrounding the entrance to the catastat, is an internal cylinder 60 open at the top. This cylinder (which in a typical case is about 12 feet in diameter and about 15 feet to 20 feet high) is provided to decrease by-passing of the fresh catalyst introduced with the feed directly into the withdrawal standpipe. The reactor is provided with a plurality (in this case two) of inlet lines for feed and fresh catalyst. These lines 19 are connected in the bottom cone just outside of the internal cylinder 60. (In the flow diagram, Figure I, the feed line is, for clarity, shown as a single line 19). The reactor is also preferably provided with a baffle 61 extending from the outer shell inward and downward to a point somewhat below the top of cylinder 60. This baffle is provided to prevent reactant vapors from channeling up the sides of the reactor and to provide more even distribution of catalyst and reactant vapors. The inlet pipe 46 for the intro-

duction of the C_9 polymers may be located in the upper portion of the catastat, as shown, or it may be at a somewhat more elevated position, for instance in the lower part of the internal cylinder. This line, since it does not handle catalyst, may be of considerably smaller diameter than the inlet lines 19. Line 46 is preferably provided with a distributing manifold 62, as indicated. The reactor is provided with various catalyst level, temperature and pressure indicators and also with such accessories as emergency aeration nozzles, etc. These, however, have no bearing on the present invention and have been omitted in Figure II.

In operation the fluid catalyst is maintained at a level such as indicated in Figure II. The hot freshly regenerated catalyst and hydrocarbon oil vapors enter the reactor via line 19 and the vapors pass up through the fluid catalyst bed. The combination of the catalyst level and rate of introduction of the reactant vapors determines the space velocity. Partially spent catalyst is continuously withdrawn from the fluidized bed through the internal cylinder 60 and the catastat 26. Since the only heat supplied to the reactor is supplied by the incoming mixture of catalyst and oil vapors (and also due to the cooling effect of the materials introduced in the catastat) the catalyst in the internal cylinder and in the catastat is at a somewhat lower temperature. The C_9 polymers introduced via line 46 and manifold 62 contact this partially spent and partially cooled catalyst in the catastat and internal cylinder and then finally contact only a portion of the main catalyst bed above the internal cylinder. Since there is a physical separation of the vapors for a distance of say 15 to 20 feet by the internal cylinder and since the cross section of the internal cylinder is much smaller than that of the reactor the overall space velocity of the C_9 polymers may be much greater than that maintained for the cracking of the hydrocarbon oil feed. The actual contact time in the case of the C_9 polymers is also considerably reduced by the steam or other gas introduced at points along the length of the catastat to maintain the catalyst therein in a free flowing condition. These gases, as pointed out above, as well as the cooling effect of the C_9 polymers and the cooling effect of the endothermic cracking reaction, tend to cool the catalyst with which the C_9 polymers are contacted. This also contributes towards providing mild cracking conditions for the C_9 polymers while allowing relatively drastic conditions for the hydrocarbon oil.

Returning to Figure Ia, the higher boiling fraction removed from fractionator 42 and consisting largely of C_4 hydrocarbons may be subjected to a separate polymerization treatment to selectively polymerize isobutylene. The conditions, catalysts, etc., for such a selective polymerization are well known and do not need to be described here. Thus, the C_4 fraction is passed via line 47 to polymerization reactor 48. The product passes to a fractionator 49. The isobutylene polymer is withdrawn by line 50 and is available for alkylation. The overhead product consisting largely of alpha and beta butylenes and isobutane is passed to an extraction distillation column 51 to separate beta butylene which is then recovered as a product of the process. The mixture of alpha butylene and isobutane remaining may then be used to alkylate the isobutylene polymers. Since the process of the invention produces large amounts of butylenes as well as increased amounts of isobutane, the production of first quality alkylate is the maximum that can be obtained without an outside source of isobutane. Thus, the production of large quantities of desired beta butylene is obtained without any decrease in the amount or quality of alkylate (which directly controls the production of 100 octane gasoline). In fact, due to the increased production of isobutane the production of alkylate may be increased somewhat.

The catalytic gasoline produced in the described process using this particular feed is not of the best quality, but may be easily converted into first quality high anti-knock aviation base stock by a simple mild hydrogenation treatment. When this material is blended with the alkylate excellent yields of first quality gasoline are produced from even very poor, refractory and contaminated feed materials, and the excellent yields of beta butylene are obtained, so to speak, gratis.

I claim as my invention:

1. A process for the catalytic conversion of hydrocarbon oils heavier than gasoline into useful normally liquid and normally gaseous products including gasoline, beta butylene and an isobutane-olefin mixture suitable for production of quality alkylate, which comprises the process steps of catalytically cracking the hydrocarbon oil in a fluid catalyst system with a finely divided cracking catalyst under conditions of temperature and space velocity to convert at least 10% of the hydrocarbon oil into normally gaseous products including propylene, butylenes and isobutane, selectively polymerizing propylene from said gaseous products predominantly to C_9 polymers, catalytically cracking said C_9 polymers simultaneously with said hydrocarbon oil at a higher space velocity thereby to produce additional quantities of isobutane and butylenes.

2. Process according to claim 1 in which the catalytic cracking of the hydrocarbon oil is carried out at a temperature of at least 1000° F.

3. Process according to claim 1 in which the hydrocarbon oil feed is a reduced petroleum.

4. Process according to claim 1 in which the hydrocarbon oil feed is a vacuum flashed distillate from a reduced petroleum having a molecular weight between about 280 and 350.

5. Process according to claim 1 in which the hydrocarbon oil feed is a mixture of virgin distillate and cracked distillate from a thermal cracking operation and the product gases from both operations are combined prior to selectively polymerizing the propylene.

6. Process according to claim 1 in which the hydrocarbon oil is catalytically cracked with a boric oxide cracking catalyst in the presence of at least two moles of steam per mole of hydrocarbon feed.

7. Process according to claim 1 in which the catalytic cracking is carried out in a bottom draw-off fluid catalyst reactor and the higher space velocity of the propylene polymer is obtained by injecting the propylene polymer into the withdrawal standpipe.

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