Sept. 25, 1973

A. J. CONNER

3,761,391

PROCESS FOR THE PRODUCTION OF GASOLINE AND LOW
MOLECULAR WEIGHT HYDROCARBONS
Filed July 26, 1971

INVENTOR
Algie J. Conner

BY:
James R. Hosten, Jr.
Robert W. Erickson
ATTORNEYS
PROCESS FOR THE PRODUCTION OF GASOLINE AND LOW MOLECULAR WEIGHT HYDROCARBONS

Algie J. Conner, Downers Grove, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill.

Filed July 26, 1971, Ser. No. 166,048

Int. Cl. C10G 11/18, 37/06

U.S. Cl. 208—76

3,761,391

3 Claims

ABSTRACT OF THE DISCLOSURE

A process for the production of gasoline and low molecular weight hydrocarbons from a gas oil feed stock which process comprises a riser type cracking step performed on a gas oil feed and the cracking of recycle gasoline materials which may take place in either a riser type reaction zone or a fluidized dense bed reaction zone. The recycle gasoline is cracked by contacting a partially deactivated cracking catalyst which has previously contacted fresh oil feed. The gas oil is cracked by contacting a freshly regenerated cracking catalyst. The process of recycling gasoline allows a higher production of olefinic C₃ and C₄ hydrocarbons which can be converted to high octane components and makes the increased production of C₅ and C₆ saturates which may be valuable in the production of LPG fuel.

BACKGROUND OF THE INVENTION

Field of the invention

The field of art to which this invention pertains is general refinery processing. Particularly this invention relates to a process for production of gasoline and low molecular weight hydrocarbons by catalyst cracking of fresh gas oil feed and recycle gasoline stocks. More specifically, this invention relates to a riser type cracking of gas oil feed stocks and the cracking of a recycle gasoline in either a riser or a dense bed reaction zone which contains partially deactivated cracking catalysts.

Description of the prior art

It is known in the cracking art that gas oils may be cracked to effect the production of lower molecular weight materials including gasoline and light hydrocarbons. In instances in which a gasoline material and light weight olefinic and saturated materials (generally C₃ and C₄ hydrocarbons) are desired, catalytic cracking of a gas oil feed stock can effect such a product distribution. In instances in which there is an increased need for olefinic hydrocarbons or light saturated hydrocarbons at the expense of the gasoline yield, the reaction conditions in the catalytic cracking zone can be altered to effect such a required product distribution.

The problem associated with cracking recycle gasoline in a reaction zone where fresh feed is present is that hydrogen transfer from the fresh feed to the olefins which are derived from the recycle gasoline causes the olefins to be saturated. Processing the recycle gasoline in a separate reaction zone over partially deactivated catalyst eliminates most hydrogen transfer from the fresh feed and allows more olefins to be produced. Hydrogen transfer occurs by the transfer of hydrogen from the fresh feed stock or higher molecular weight cracked components to the particular olefin which is being produced. In instances where the C₃ and C₄ olefins are saturated their octane potential is decreased due to the fact that most of the C₃ and C₄ paraffins are not easily reacted via alkylation to form valuable gasoline components with the exception of the C₄ paraffins.

Another advantage of using a separate reaction zone to crack recycle gasoline is that less coke is made per unit conversion of the recycled gasoline when partially deactivated catalyst is used. The use of partially deactivated catalyst in the second reaction zone prevents extensive degradation of light olefins products via polymerization which is enhanced by active acidic fresh catalysts. The partially deactivated catalysts are not as acidic as freshly regenerated catalysts and therefore reduce polymerization side reactions.

SUMMARY

The invention can be summarized as a process for the catalytic cracking of a gas oil feed stock in a riser reaction zone and the cracking of a recycle gasoline stream by partially deactivated catalyst in a separate reaction zone. The cracking of the gas oil feed stock and the recycle gasoline take place at relatively high temperatures.

It is a specific object of the present invention to provide a catalytic cracking process wherein the gasoline stream is recycled to a catalytic cracking reaction zone in which partially deactivated cracking catalyst is present to effect the production of large quantities of C₃ and C₄ olefinic hydrocarbons.

BRIEF DESCRIPTION OF DRAWING

The attached drawing shows one particular mode of operation for the production of gasoline and relatively large yields of light gaseous hydrocarbons. The vessels shown in the attached drawing are labeled as follows: Gas oil riser reaction zone 1, cyclone separation zone 2, recycle reaction zone 3, regeneration zone 4; and separation means 5.

Fresh feed is passed into the process via line 7 at a given rate, and when required at preheated temperatures, into line 6 which enters the gas oil riser reaction zone 1 at its lower portion. Line 6 and riser reaction zone 1 may be a single long vessel generally having a large length over diameter ratio and in many cases are identical in size. Freshly regenerated catalyst from regeneration zone 4 which has had substantially all of the carbon present on it burned off in regeneration zone 4, leaves that zone via line 8 and contacts the fresh feed at the intersection of line 6, 7 and 8. The point at which lines 6, 7 and 8 meet is designed in such a manner that the regenerated catalyst vaporizes hydrocarbons which contact it. The vapors carry the catalyst up through line 6 into, through, and out of riser reaction zone 1 directed into a cyclone separation means 2. Cyclone separation zone 2 may be located within a vessel in which the recycle reaction zone 3 is located or, as indicated by the drawing, a separate vessel from the recycle reaction zone. Cyclone separation means 2 may consist of any number of cyclones in parallel or serial arrangement in order to effectively separate partially deactivated catalyst and oil from the effluent leaving the riser reaction zone 1.
The hydrogen effluent which is separated from the partially deactivated catalyst flows through line 18 into separation zone 5. The partially deactivated catalyst passes from cyclone separation zone 2 via line 19 into the recycle reaction zone 3. In instances when the recycle reaction zone contains a dense fluidized bed of catalyst, it is generally located between the riser reaction zone and the catalyst regeneration zone. The recycle reaction zone 3 has a recycle stream passing to it which comes from separation zone 5 via line 12 through valve 11. The recycle gas stream contacts a partially deactivated catalyst at conditions to effect partial cracking of gasoline to light “straight run” gas or paraffins which are subsequently removed from this zone via line 20. Not shown in the drawing but of significance is a cyclone separation means which is generally required to separate the hydrocarbon effluent and catalyst which are withdrawn from the recycle reaction zone. The cyclone separation means may be located within the recycle reaction zone or externally to it. The catalyst which leaves the recycle reaction zone passes into the regenerator via line 21. The recycle reaction zone may be utilized in the form of a riser reaction zone. In these instances the partially deactivated catalyst leaving the cyclone separator 2 passes into a vessel with feed stock passing upward. The catalyst contacts recycle gas causing it to vaporize and carry catalyst up through the riser. When cracking of the gasoline occurs. The catalyst and hydrocarbon leaving this riser then pass into a cyclone separation zone and are separated from the cracked gas. The oil passes to another separation zone 5 or another separation zone. The spent catalyst can then be stripped and returned into the regenerator 4. Separation zone 5 is generally a fractionator of known design familiar to those associated with the refinery arts. It generally has outlet points for removing various products from this zone. The gas cycle oil or heavy cycle oil or both may be hydrogenated prior to passage into riser 1 to partially saturate rings in the polycyclic aromatics which can then be broken via cracking. This allows increased production of alkyl aromatic hydrocarbons such as toluene or xylene which are high octane components substantially boosting the octane rating for the gasoline produced.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Riser type reaction zones are well known to those versed in the cracking art. Typically, a riser reaction zone is an elongated cylindrical vessel having a large length to diameter ratio having a feed and catalyst inlet at a bottom portion thereof and a catalyst and oil effluent outlet at the top. In this specification, dilute phase riser operating conditions are defined as those conditions in which a feed stock and catalyst are concurrently passed through a riser type reaction zone with the catalyst density in the riser maintained somewhere between 1 up to about 20 pounds per cubic foot. The gas oil riser reaction zone refers to a riser reactor in which gas oil feed is cracked with freshly regenerated catalyst. In this specification, dense phase catalytic cracking operations include a fluidized bed of catalyst located within a vessel with feed stock passing upward and bubbling through the fluidized bed of catalyst causing a reaction to occur. The feed stocks pass upward through the bed. The catalyst particles remain in the fluidized bed. When a continuous supply of deactivated catalyst passes into the bed, a catalyst draw off is utilized at the lower portion of the bed. Thus, it can be seen that in the dense phase fluidized catalytic cracking, the flow of hydrocarbons with respect to catalyst in the bed is generally in a counter-current direction, where there is continuous feed and catalyst supplies. The dense phase bed of fluidized catalyst generally has a density greater than about 20 lbs. per cubic foot in order to prevent an extreme amount of catalyst from being entrained in the hydrocarbon material passing out of the fluidized bed of catalyst.

The recycle reaction zone may include both a dilute phase riser operation or a dense phase cracking operation. Fresh catalyst generally is catalyst passing out of the regeneration zone which has not had the opportunity to contact a hydrocarbon stream before contacting the gas oil feed stock in the process. Partially deactivated catalyst is cracking catalyst which has contacted gas oil feed in the first riser reaction zone and which has deposited thereon a quantity of coke or carbon. In most instances it is required that the partially deactivated catalyst contain sufficient activity to at least cause substantial reaction of the recycle gasoline which contacts it in the recycle reaction zone. The catalyst which leaves the recycle reaction zone can also be termed "partially deactivated catalyst," since this catalyst contains a greater quantity of coke or carbon on it than a catalyst which leaves the regeneration zone. The gas oil feed stocks which can be used in the process of this invention can comprise any hydrocarbon material capable of producing gasoline boiling range hydrocarbons which are being subjected to normal catalytic cracking conditions. The feed gas oils may be obtained from various crude sources. They have boiling ranges anywhere from about 400° F. up to and including 1200° F. by ASTM method D-1160. Particularly suitable feed stocks include distillates from gulf coast and mid-continental crudes which have Conradson carbon residue below about 1.5 wt. percent. In many instances the feed stocks range from the first riser reaction zone can contain heavy cycle oil or light cycle oil or quantities of both which are recycled to the process as is typically done in catalytic cracking operations. The term gasoline or recycle gasoline shall refer to cracked products which have boiling ranges of from about 100° F. up to and including 450° F. Typically, gasolines include hydrocarbons of the aromatic and alkyl-aromatic variety along with iso- and normal olefins and
3,761,391

5 paraffins and in some instances cyclo-paraffins. In some cases the gasoline recycled to the recycle reactor may be a heart cut of the gasoline withdrawn from the main column.

The term "dry gases" shall include hydrogen and the \( \text{C}_2 \) and \( \text{C}_3 \) hydrocarbons. Typically the dry gases contain components which are not valuable in refinery operations and hence in this process are desired to be minimized. They are generally the product of demethylation or de-ethylization of aromatics or the products of thermal or free radical cracking and should take place in the recycle reactor.

The term LPG refers to liquid petroleum gases and is generally synonymously used with the term light gases in a refinery art. The liquefied petroleum gases generally include propane or iso- or normal butane or combinations thereof. Typically, these components are relatively valuable in refinery processing as they are easily used in the fuel market. Included within the LPG components are the \( \text{C}_3 \) and \( \text{C}_4 \) olefins and the \( \text{C}_3 \) and \( \text{C}_4 \) paraffins. In many instances the light gases produced by this process are very valuable in producing high octane components in the form of alkylate gasoline. The \( \text{C}_3 \) and \( \text{C}_4 \) olefins are readily alkylatable with isobutane which is produced in high yield in this process. The \( \text{C}_3 \) paraffin is typically not alkylated.

There are a large number of catalysts suitable for use in catalytic cracking such as silica-alumina, silica-magnesia, silica-zirconia, acid activated clay, crystalline catalysts including faujasites dispersed in a silica containing inorganic oxide matrix, montmorillonite or the zeolite family of catalyst either dispersed in a silica containing matrix or an alumina containing matrix or used in pure form, the type X and type Y structured zeolites having certain cations including the rare earths exchanged thereon and used as a catalytic cracking catalyst in admixture with an amorphous catalyst, crystalline catalysts of the type X or type Y variety in a silica or an alumina matrix. Specially active catalysts which find much use presently in the catalytic cracking operation are those amorphous silica-alumina catalysts having concentrations of about 10 to 40 wt. of alumina and 90 to 60 wt. of silica, or those having 2 to 20% of a type X, Y or faujasite structured material dispersed in a silica or in a silica-alumina matrix. Other suitable catalysts include the decalcination form of the type X or Y structured zeolites.

Typical, gas oil cracking conditions including temperatures of from about 800° F. to about 1275° F., pressures of from about atmospheric up to 50 p.s.i.g., catalyst to oil weight ratios of from about 1 to about 20 and combined feed ratios (fresh feed plus recycle material divided by fresh feed) of from about 1 to about 3.0. The fresh feed may be mixed with recycle heavy oil or light cycle oil or a slurry oil. Gasoline cracking conditions include the contacting of recycle gasoline and, in some instances, a gasoline material either from another processing unit, with a partially deactivated catalyst at conditions to produce light gas and gasoline. Partially deactivated catalyst should be the sole catalyst effecting gasoline cracking operations. A portion or all of the partially deactivated catalyst leaving the gas oil riser can pass into the recycle reaction zone.

Specific gasoline cracking conditions include pressures of from about atmospheric up to about 20 p.s.i.g., temperatures of from about 950° F. up to about 1300° F. and combined feed ratios of from about 1 to 2. The combined feed ratio described can be utilized when part of the effluent from the gasoline cracking zone is recycled back to that zone.

When the gasoline is cracked in a riser type cracking zone the weight hourly space velocity (WHSV) can vary from about 15 hr.\(^{-1}\) up to about 120 hr.\(^{-1}\). The optimum gasoline cracking would take place at about 2 to 10% contact time of catalyst and fresh feed to the gasoline riser. The catalyst to oil ratio (C/O) based on fresh feed to the gasoline riser may vary from about 2 up to about 15 or 20.

6 In instances in which gasoline in cracked in a dense bed cracking zone the WHSV can vary from about 1/4 up to about 20 or higher.

The gas oil may be cracked at gas oil cracking conditions including a WHSV of from riser-type cracking zone about 100 or higher based on fresh feed. Again the optimum catalyst and oil contact times based on fresh feed should be around 4 seconds.

The gas oil cracking conditions should be limited to those operations in which a dilute phase riser-type reaction zone is utilized. It is preferable that the gas oil cracking conditions include the use of a riser-type cracking zone which is connected directly to a cyclone separation unit in order to quickly and efficiently separate cracked gas oil feed stocks from partially deactivated catalyst in order to prevent gas oil feed stocks from passing through a relatively dense bed of partially deactivated catalysts. The gasoline cracking conditions can include both the use of a dilute phase riser or a dense phase cracking operation.

In normal operations, the freshly regenerated catalysts and gas oil feed stocks are passed into a riser reaction zone at its lower end at conditions in which fresh feed and any recycle material are vaporized and carry all of the catalysts up through the riser with the conversion of at least a portion of the feed stock into gasoline lighter and heavier weight hydrocarbons. Typically at the uppermost portion of the riser-type reaction zone there is a cyclone separation zone of one or more cyclones in series or in parallel. The separation zone effects the immediate separation of a partially deactivated catalyst and reaction products from the gas oil riser. The reaction products pass into a fractionation zone wherein they are separated into dry gas, light gases, gasoline and cycle oil. A part or all of the partially deactivated catalyst passes into the recycle reaction zone.

After the partially deactivated catalyst has contacted the recycle gas oil, it is then passed to the regeneration zone. The regeneration zone causes the coke deposited on the catalyst to be burned off so it can be reused as freshly regenerated catalyst.

The gas oil riser can vary anywhere from a few feet to as many as a 100 or more feet in length and have diameters ranging from a few inches up to 5 or more feet in diameter. In cases in which the recycle reaction zone is a riser type reactor it can be of the same design as the gas oil riser except it will probably be smaller in overall dimensions than the gas oil reactor.

In instances where the recycle reaction zone contains a dense bed of fluidized catalyst a reaction vessel is necessary to hold the catalyst. Typically, this vessel has a large diameter and generally has a low ratio of its length to diameter in order to allow the partially deactivated catalyst to build up within the lower portion of the vessel. Gasoline is allowed to pass into the vessel at a lower portion thereof to contact the bed of partially deactivated catalyst.

The following example is presented to illustrate the advantages gained by employing the process of this invention and is not presented as an undue limitation upon the scope of the attached claims.

**EXAMPLE**

The equipment used in this example consisted of an 85-foot long riser which was made up from a 3 1/2 inch diameter schedule 80 stainless steel pipe. The riser was connected to a cyclone separator which separated catalysts from hydrocarbons which were leaving the riser. The cyclone dipleg was connected to the recycle reactor which was a small vessel which contained a fluidized bed of the partially deactivated catalyst which had passed through the riser. The riser had a 4 1/2 inch diameter inlet line located at its lowermost portion. A gasoline recycle inlet stream passed into the reactor through its side near the bottom of the vessel. At the top of the pot was a hydrocarbon outlet which itself was contacted with a
cylcone separator, which in turn was connected to the hydrocarbon outlet of the gas oil riser cyclone. The hydrocarbon effluent leaving the boil oil riser and the recycle reactor passed to a knock-out pot before passing into a pilot scale main column. The catalyst leaving the recycle reactor, passed through the recycle reactor in order which steam contacted the catalyst in a countercurrent fashion to strip any hydrocarbons from the spent catalyst which was then passed into the regeneration zone. The regeneration zone was operated at conditions to effect the removal of the majority of coke deposit on the catalyst passed into the regeneration zone. Freshly regenerated catalyst passed out of the regeneration zone and directly into the bottom portion of the 85-foot long riser where it contacted the fresh feed stock, which passed through the plant.

All of the hydrocarbons leaving the process after passage through the knock-out pot were then passed into a main column where they were separated into various streams such as a hydrogen and dry gas stream, a C6 and C4 LPG stream, a gasoline stream, a bottoms and cycle oil streams. The gasoline before being recycled back to the recycle reactor was debutanized to yield an essential C6 through 430° end point gasoline.

The catalyst used for the experiments was the same for both the once-through operation and the gasoline recycle operations. It was a rare earth exchanged type Y crystalline aluminosilicate catalyst which had been equilibrated through process use. During the once through operations the fresh feed gas oil stream was passed through the 85-foot riser in admixture with freshly regenerated cracking catalyst. The catalyst and oil were passed into a cyclone where they were separated. The hydrocarbon effluent was passed to the main column where the various components of the effluent were separated and analyzed in order to determine a once through yield structure. During the once through operations there was no recycle of heavy, light cycle or bottom oils to the riser reaction zone. There was also no recycle of gasolines to the recycle reactor during these operations.

During the gasoline recycle operations a gas oil feed stock was passed through the riser reaction zone. There was no recycling of cycle oils or bottom oils to the riser. The riser effluent was passed into the main column where it was separated and analyzed to yield structure. A portion of the gas material withdrawn from debutanizer was recycled back to the recycle reactor in order to obtain yields using a flow pattern according to the process of this invention.

The gas oil feed stock for both the once through and recycle operations was the same and was made up of a blend of gas oils having the properties as shown in Table I below.

### TABLE I—YIELDS

<table>
<thead>
<tr>
<th>Operations</th>
<th>Once through (light)</th>
<th>Gasoline recycle (heavy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh feed riser temp. °F</td>
<td>1,030</td>
<td>1,028</td>
</tr>
<tr>
<td>Recycle gasolene riser temp. °F</td>
<td>667</td>
<td>667</td>
</tr>
<tr>
<td>WHSV (FF riser) hr⁻¹</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>CPE</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>80.0</td>
<td>80.3</td>
</tr>
<tr>
<td>Yield, on fresh feed:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2, weight percent</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>H2O, weight percent</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>C4, weight percent</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>C5, onilin, weight percent</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>C6, paraffin, weight percent</td>
<td>2.3</td>
<td>4.8</td>
</tr>
<tr>
<td>C7, olefin, weight percent</td>
<td>0.6</td>
<td>15.4</td>
</tr>
<tr>
<td>C8, paraflin, LV percent</td>
<td>6.2</td>
<td>9.2</td>
</tr>
<tr>
<td>nC6, paraffin, LV percent</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>C7 onilin, LV percent</td>
<td>0.0</td>
<td>12.2</td>
</tr>
<tr>
<td>C8 to 430°F gasoline, LV percent</td>
<td>62.6</td>
<td>40.2</td>
</tr>
<tr>
<td>Bator and cycle oil, LV percent</td>
<td>20.0</td>
<td>10.7</td>
</tr>
<tr>
<td>Coke, weight percent</td>
<td>4.1</td>
<td>6.9</td>
</tr>
<tr>
<td>Gasoline IGN (closed)</td>
<td>53.2</td>
<td>58.7</td>
</tr>
<tr>
<td>Total C6 and C7 (lpg), LV percent</td>
<td>28.2</td>
<td>41.3</td>
</tr>
<tr>
<td>C8 distillate/total C8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>C9 to total C9</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

For both the once-through and gasoline recycle operations above the conversions were held relatively constant. This meant that the same essential quantity of bottoms and cycle oils were produced as yield on fresh feed.

As can be seen from the above data, the gasoline recycle operation allows an increased amount of LPG based on feed stock with the resulting increase in octane number of the remaining C6 to 430 gasoline. The operations in which no recycle gasolene was utilized produced a significantly lower amount of LPG products and a gasoline having a lower octane rating than that obtained by using the gasoline recycle operation. It must be pointed out, however, that the total gasoline yield from the once-through operations was higher as would be expected when compared to the operations in which gasoline was recycled to the reactor part.

An additional advantage of using gasoline recycle operations is that the gasoline remaining after the recycle gasolene has been cracked is of a higher octane than the gasoline produced on normal cracking operations in which gasoline is not recycled.

I claim as my invention:

1. A process for the production of gasoline and low molecular weight hydrocarbons which process comprises the steps of:

   (1) contacting a fresh feed gas oil stream with a freshly regenerated cracking catalyst in a gas oil riser reaction zone at gas oil cracking conditions to effect the production of reaction products including gasoline and light hydrocarbons and the partial deactivation of said freshly regenerated catalyst.

   This also means that the catalyst is still active after this process.
passing said reaction products and partially deactivated catalyst leaving said riser reaction zone directly into a cyclone separation means at separation conditions to effect the separation of said partially deactivated catalyst from said reaction products,

(3) separating gasoline product from said reaction products,

(4) passing partially deactivated catalyst into a recycle reaction zone,

(5) recycling at least an aliquot portion of said gasoline product through said recycle reaction zone at gasoline cracking conditions to effect the conversion of at least a part of said gasoline to low molecular weight hydrocarbons, and

(6) removing said low molecular weight products from said recycle reaction zone.

2. Claim 1 further characterized in that said recycle reaction zone contains a dense fluidized bed of partially deactivated catalyst.

3. Claim 1 further characterized in that said recycle reaction zone is a riser type reaction zone.

References Cited

UNITED STATES PATENTS

3,630,886 12/1971 Deed et al. ------------ 208—96
3,284,341 11/1966 Henke et al. ------------ 208—120

DELBERT E. GANTZ, Primary Examiner
G. E. SCHMITKONS, Assistant Examiner

U.S. Cl. X.R.

208—Dig. 2, 77, 113, 120, 164; 252—417