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CATALYTIC OIL CRACKING WITH AIR

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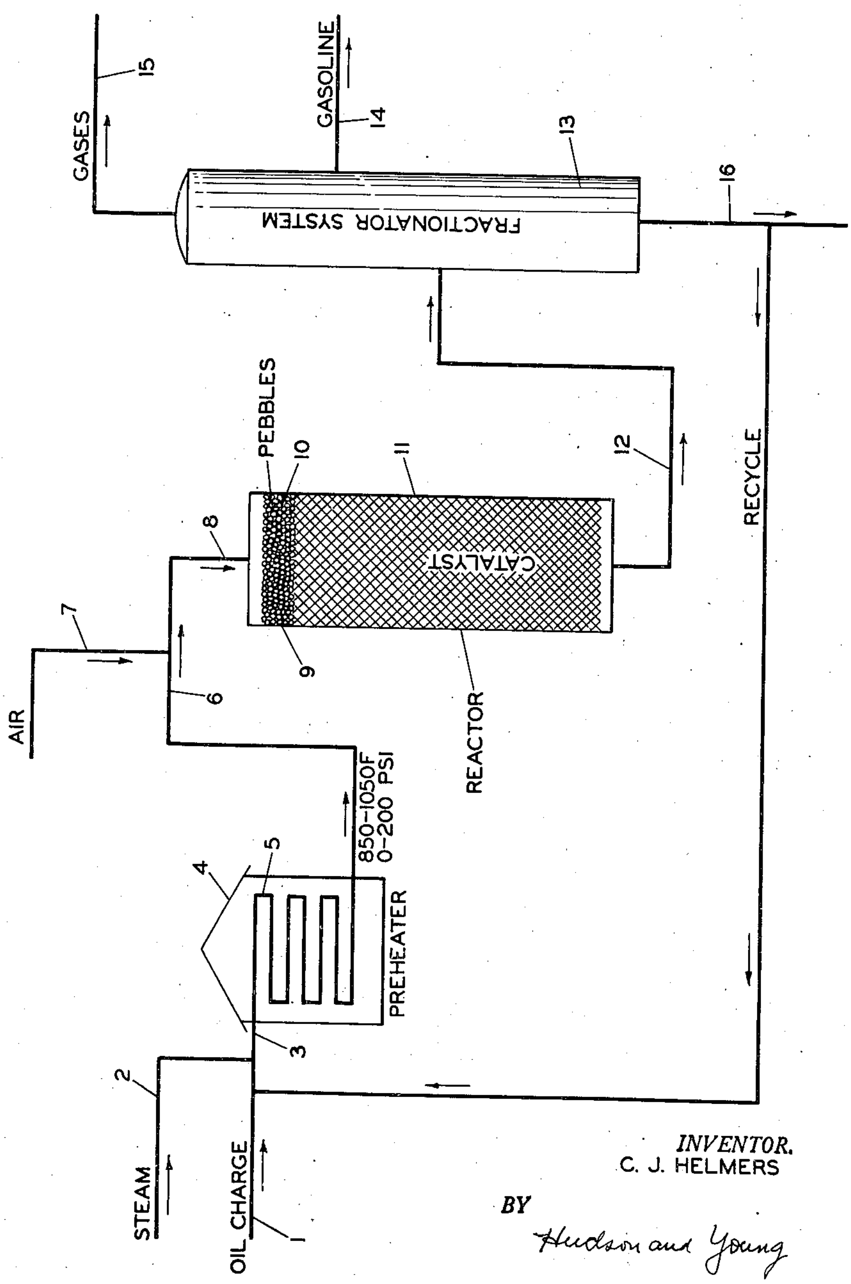

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CATALYTIC OIL CRACKING WITH AIR

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1 Claim. (Cl. 196—52)

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The present invention relates to the catalytic conversion of hydrocarbon oils. More particularly, it relates to a novel process for cracking or otherwise converting relatively heavy hydrocarbon oils in a manner which will simplify preheating of the oil and permit maintenance of more uniform cracking temperatures within the catalyst bed.

In the catalytic cracking of hydrocarbon oils, such oils are ordinarily vaporized and preheated to conversion temperatures in a preheating furnace which is usually of a tubular type. Where the feed comprises heavy hydrocarbon oils, due to the high temperatures required to vaporize the highest boiling components of the feed, excessive thermal cracking, accompanied by the formation of coke in the furnace tubes is sustained in the preheater. This thermal cracking and coke formation represent an economic loss, and in addition require frequent cessation of operations for the purpose of cleaning or burning out the furnace tubes to remove coke deposits and avoid restriction of flow and impairment of heat transfer efficiency in the preheater. Addition of steam is sometimes employed in the preheating furnace to assist in vaporization of the feed but this expedient increases the vapor volume going through the coils, and thereby increases pressure drop and the average coil pressure. This increase in pressure also tends to repress the vaporization of the high-boiling constituents.

In accordance with the present invention, the foregoing difficulties are overcome by preheating the feed to a temperature such that at least a portion of the highest boiling constituents is not vaporized, and introducing the incompletely vaporized material into the cracking zone along with a desired proportion of oxygen-containing gas. In this manner controlled oxidation of a portion of the hydrocarbon feed will occur within the reactor with a resultant increase in the temperature to a point sufficient to effect vaporization of the unvaporized components. It has further been found that in a mixture of heavy hydrocarbons and air oxidation does not effectively take place until a surface is supplied on which the oxidation reaction can proceed. For this reason the oxidation will occur within the catalyst bed, and thus vaporization of the oil will also occur within the bed accompanied by cracking and carbon deposition on the catalyst. It has further been found that in introducing the oxygen and hydrocarbon at the inlet to the bed in the manner described herein, localized combustion at the inlet will not occur as might be expected, but that there

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is an even distribution of the temperature rise due to combustion, throughout the catalyst bed. While the catalyst itself will serve as a satisfactory surface for the combustion, it has been found preferable to interpose a layer of relatively inert refractory material between the catalyst and the inlet and permit the partial combustion to take place on the surface supplied thereby. In this manner the vaporization of the feed may be completed on the inert surface and less difficulty is encountered with pressure drop caused by increased carbon deposit on the catalyst, while at the same time the catalyst activity is maintained at a higher level.

It is therefore, an object of the present invention to provide a process for the catalytic cracking of hydrocarbons wherein complete vaporization of the feed is effected without causing excessive cracking and carbon deposition in the vaporizing or preheating means. It is a further object of the present invention to provide a process for the catalytic cracking of hydrocarbons wherein at least a portion of the endothermic heat loss is supplied by partial combustion of the feed in such a manner that the heat thus supplied is uniformly distributed throughout the catalyst bed.

In one specific embodiment of my invention, the charge oil is heated in a minimum time in the preheater under conditions such that only about 75 to 90 per cent of the oil is vaporized at the preheater coil outlet. One of the points in a preheater where coking is most troublesome is that point where the last small portion of the oil is vaporized. In this method of operation, this point is not encountered in the tubes of the preheater. If air is mixed with the heated oil at some point between the preheater outlet and the reactor, the additional heat necessary for the cracking will be supplied by oxidation at the catalyst surface, i. e., at precisely the point where it is needed. It is advantageous to provide an inert surface, such as magnesite pebbles or the like, where oxidation can take place to supply the heat necessary to complete the vaporization, particularly when a relatively heavy oil is being charged and the amount of liquid hydrocarbon entering the reactor is 20 per cent or higher. By completing this vaporization on the inert surface, less difficulty is encountered with pressure drop caused by carbon deposits and the catalyst activity is maintained at a higher level. However, it is also an advantage of this process that the oxidation takes place throughout the contact mass and is not a localized reaction at the first surface contacted.

The invention may be described with reference to the attached drawing which illustrates a reactor and flow sheet for practicing the invention. The heavy hydrocarbon to be cracked which may be gas oil, or a similar high boiling oil is charged to preheater **4**, via lines **1** and **3**, with or without added steam from line **2**. This charge is heated to a suitable temperature, say in the range of 850 to 1050° F. in coil **5** with a pressure in the range of zero to 200 p. s. i. At the preheater coil outlet the incompletely vaporazied material is removed through line **6** and air from line **7** is introduced therein a suitable amount, for example in the range of 10 to 600 cubic feet per barrel of charge. The air-hydrocarbon mixture flows into reactor **9** wherein it contacts a layer of inert, heat-resistant, granular, non-catalytic material **10** disposed above the catalyst bed **11**. The catalyst may be bauxite, activated clay, or other well known catalyst suitable for the purpose. The inert material may be magnesite pebbles or any like refractory material with a relatively low adsorptive power. This material may also be in the form of granules of any desired configuration instead of pebbles. Partial combustion of the hydrocarbon charge occurs on the surface of the inert material with a resulting increase in temperature of the feed to a desired level. The liquid remaining in the charged mixture is thereby vaporized in this zone by heat liberated in the action of the oxygen with the hydrocarbon or with previously deposited carbon which may be present on the material. The thus heated vapors then pass on through catalyst bed **11** under cracking conditions. The effluent vapors are removed by line **12** and introduced into a fractionator **13** from which gasoline is separated through line **14**, light gases through line **15**, and heavy and unconverted material through line **16** for recycle to the preheater or removal from the system.

The inert material is preferably disposed in a layer adjacent to the catalyst bed, and in the case of a vertical bed will be at the top or bottom depending on the position of the inlet. The inert material may also be disposed in a separate bed or chamber in direct communication with the catalyst chamber if desired, but optimum results are achieved where a single continuous bed is formed.

This process permits inclusion of much higher-boiling material than the usual in the charge to the catalytic unit since excessive preheater coking is avoided in vaporizing the liquid hydrocarbon charge. The efficiency of utilization of the added oxygen in the process is as high as 90 to 95 per cent.

Examples

In three comparative runs, a heavy gas oil was cracked by passing it downward through a vertical catalyst chamber containing calcined bauxite. This gas oil had an API gravity at 60° F. of 31.0 and had the following ASTM distillation characteristics:

	° F.
First drop	538
10% cond	632
30% cond	667
50% cond	691
80% cond	723
90% cond	730
End point	736

The charge rate was 11.6 barrels per hour. The oil space velocity through the chamber was 1.7 liquid volumes per volume of catalyst per hour. The charge was diluted with 60 pounds of steam per barrel of oil. The pressure was 85 p. s. i. In the first run no air was added to the charge. In the second run, 2500 cubic feet of air per hour was charged at the inlet of the catalyst chamber.

The following data were obtained:

Table I

Run	1	2	3
Air Injected, cu. ft. per hr	None	2,500	None
Reactor Temperatures, °F.:			
Inlet	935	936	953
8¾ in. below inlet (top of bed)	934	953	948
11¾ in. below inlet	928	949	948
17¾ in. below inlet	910	936	923
23¼ in. below inlet	917	942	930
28½ in. below inlet	898	922	908
36¼ in. below inlet	890	917	901
44½ in. below inlet	885	909	895
49 in. below inlet	883	908	893
54¼ in. below inlet (bottom of bed)	881	900	895
Outlet	827	848	832
Average bed temperature	903	926	915
Conversion, vol. per cent of charge	19.1	32.0	21.2

In comparing runs 1 and 2, the inlet temperature was the same, but in the first section of the bed in run 2, a temperature increase was effected by partial combustion with air. This served to effect complete vaporization of the oil and the resulting increase in average temperature gave an increase in conversion from 19.1% to 32.0%. The product composition from all three runs was about the same.

Run 3 was carried out at a higher initial temperature in the absence of air, and demonstrates the effect of adding air at the inlet as in run 2 in raising the temperature in the various portions of the bed and in raising the average temperature of the bed. The conversion in run 2 was 32.0 as against 21.2 in run 3.

In another series of runs a topped crude-gas oil blend having an API gravity of 29.2 was cracked. Four runs were made at a feed rate of 8 barrels of oil and about 15 pounds of steam per barrel of oil per hour. The process period for each run was 3 hours. Runs 4 and 5 were made without injecting air, and runs 6 and 7 were made while injecting about 100 cubic feet of air per barrel of feed. Before runs 6 and 7, the chamber was opened and 9 inches of catalyst were removed from the top of the bed and replaced with a corresponding volume of ceramic pebbles. The chamber contained 3211 pounds of catalyst in the runs without pebbles and 2954 pounds in those with 9 inches of pebbles.

The results of these runs are summarized in the following table:

Table II

Run	4	5	6	7
Air cu. ft./bbl	0	0	108	109
Reactor Temp., ° F.:				
Inlet temp	928	950	950	911
Top of catalyst bed	868	885	[1] 1,018	[1] 1,042
11¼ in	868	896	993	944
17½ in	869	889	931	875
29 in	874	891	921	882
45 in	868	877	904	871
78½ in	855	865	890	854
Bottom of bed	839	866	897	852
Conversion (vol. per cent of charge)	25.13	25.90	34.92	24.60

[1] Top of catalyst bed—9 inches of pebbles above catalyst.

The results in Table II demonstrate the temperature effect resulting from combustion in the pebble layer, with increased temperature and vaporization of feed. The temperature rise due to combustion in the pebble layer is evenly distributed in the catalyst bed, with resulting increase in percentage of conversion.

I claim:

A process for the catalytic conversion of a hydrocarbon oil containing as a minor portion constituents capable of forming coke upon complete vaporization thereof which comprises preheating said oil to a temperature such that substantially all of the non-coke forming but substantially none of the coke forming constituents of said oil are vaporized, admixing all of said preheated oil with an oxygen-containing gas, contacting all of the resultant mixture with a bed of inert, non-catalytic, granular heat resistant material and effecting therein combustion of said hydrocarbon oil to elevate the temperature to a point sufficient to effect complete vaporization of said hydrocarbon including said coke-forming constituents, and then contacting the completely vaporized mixture with a contiguous bed of cracking catalyst under cracking conditions to crack said hydrocarbons.

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