

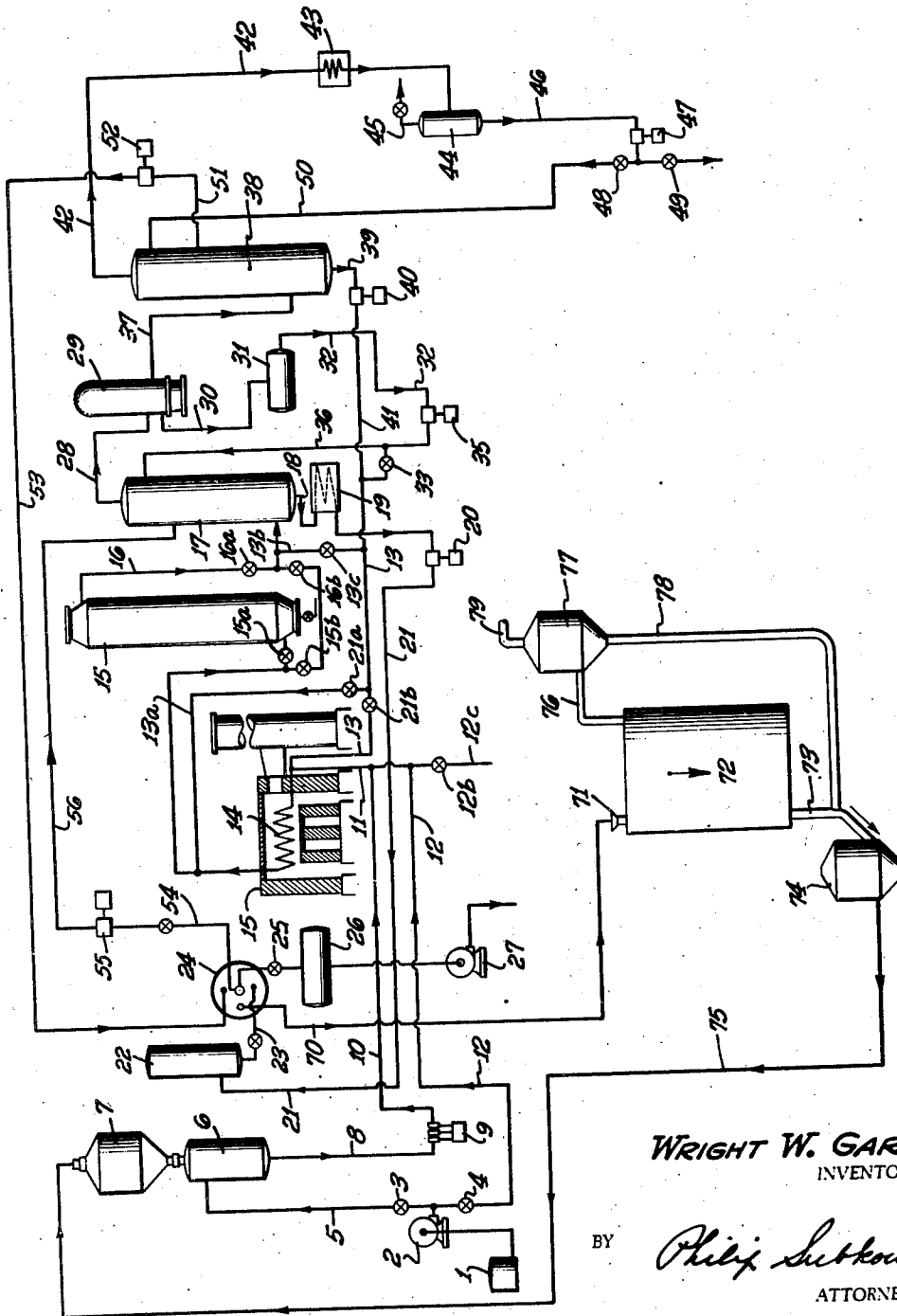
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CATALYTIC CRACKING PROCESS WITH SUSPENDED CATALYST

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## CATALYTIC CRACKING PROCESS WITH SUSPENDED CATALYST

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1

The so-called suspensoid cracking process comprises suspending a solid contact material in the liquid oil to be converted, subjecting the oil and the contact material to cracking conditions in cracking coils, separating the generated vapors from the residual fractions containing the contact material, and then separating the contact material from the residue by filtration. It is understood, of course, that the term "suspensoid" as herein employed is used in the sense understood in the catalytic cracking art and not the technical sense of colloidal chemistry.

The function of the contact material is to present surfaces upon which carbonaceous material and coke formed in the process may be deposited and thus prevent the deposit of the coke on the heated surfaces of the coils. This feature of the process permits the attainment of oil-cracking temperatures in excess of the temperatures permissible when cracking oil without such contact material.

Thus, in cracking oils having fractions boiling in excess of about 700 to 750° F., permissible temperatures and cracking times must be limited to avoid excessive coke deposit. Temperatures above about 925 to 950° F. are usually not practical because of such excessive coking. By employing suspensoid cracking, oils containing fractions boiling in excess of 650° F., and even oils containing residual fractions, may be cracked at temperatures about 100° F. higher than that permissible when converting such oils without such contact material. The resultant process yields higher conversions per pass and also increases the anti-knock rating of the gasolines.

The contact materials which are employed, since they act primarily as foci for deposit of coke, are usually inert solids such as inert clays or are weakly catalytic material. Such materials require the relatively high temperatures of suspensoid cracking in order to obtain commercial yields of gasoline of the required octane rating. The gasolines formed are, however, of high aromaticity and do not have good tetra-ethyl lead susceptibility.

I have found that the suspensoid process may be materially improved both in yield of gasoline per pass and in anti-knock rating of the gasoline produced, and also that the isobutane, isobutylene, and butylene content of the cracked gases may be increased over that of the suspensoid process employing non-catalytic or weak catalytic contact material, by employing a superactive catalyst. I can by this means lower the cracking temperature below that employed by

2

ordinary suspensoid cracking temperature, i. e., to that usually employed in thermal cracking, that is, in the neighborhood of 900 to 950° F. By increasing the equivalent cracking time above that employed in ordinary suspensoid cracking, I may, in my process, also increase the anti-knock rating and tetra-ethyl lead susceptibility of the resulting cracked gasoline.

By operating at the lower temperatures made possible by the use of the superactive catalysts, I am enabled to produce a high yield of gasoline which is iso-paraffinic in nature. This gasoline has a high anti-knock value in the unleaded state and also has a higher tetra-ethyl lead susceptibility than the aromatic gasoline obtained in the ordinary suspensoid cracking.

In suspensoid cracking it is the practice to discard the contact material which has been filtered from the residue. In my process the catalyst, after it is filtered from the residue, is regenerated by controlled combustion of the coke deposited on the catalyst. In my process it is preferable to employ catalysts of small particle size, such as powdered granular material to obtain maximum contact surface. It is, however, not desirable to employ material which is preponderately less than about 20 microns in size. I prefer to employ a material which contains but a minor amount of material which is less than 20 microns in size. Substantial quantities of extremely fine material will not readily separate out in the residue, but will be carried by the vapors and clog the vapor passages and trays of the rectifying towers employed in the process. The superactive catalysts which I employ have a tendency to be ground down to finer sizes due to the abrasive action in the process. This abrasion, where it occurs against the surfaces of the metallic tubes and containers, tends to contaminate the catalyst with fine particles of iron and iron oxide. Such materials tend to reduce the efficiency of the catalyst. By controlling the velocity of the gases traversing the regeneration furnaces employed in my process, I am able to separate the material finer than 20 microns and the particles of iron and iron oxide and discharge them with the gases from the furnace, and thus continuously purify and automatically size my catalyst.

This invention will be further understood by reference to the description and the drawing illustrating my process.

The oil to be cracked contained in container 1 may be a gas oil and preferably one boiling within the range of 400 to 550 or 600° F., such as one having an average boiling point of 525° F. On the

other hand, it may be a heavy distillate cracking stock. The oil is passed by pump 2 and split by control of valves 3 and 4. Part of the oil passes through line 5 into the slurry tank 6. The catalyst is contained in bin 7 and discharges in controlled amounts into the slurry tank 6.

I prefer to employ high activity catalysts such as an acid treated sub-bentonite, treated to a degree sufficient to produce a material containing from about 10 to 20%  $Al_2O_3$  and preferably from 15 to 20% of  $Al_2O_3$  calculated upon volatile free material. I may employ such a material modified by deposit of hydrated alumina on the material by reacting a mixture of said clay and soluble aluminum salts with an alkali metal hydroxide or preferably with ammonium hydroxide and washing free of alkali and soluble salts. I may employ a mixed silica alumina gel formed by reacting sodium silicate with a soluble aluminum salt, such as aluminum sulphate, aluminum chloride, or by acidifying mixtures of sodium aluminate and sodium silicate and washing free of salts and drying the catalyst. Such catalysts are characterized by their high activity in cracking petroleum. For example, such catalysts will show from 4 to 6 or more times the catalytic activity (measured in terms of gasoline yield) than the native sub-bentonite or fuller's earth or other inert material exhibits in cracking under like conditions.

I mix the catalyst with the oil in amounts to give a total catalyst to oil ratio at the entrance to the cracking coil, as will be later described, of from about 3 to 10%, for example, about 5% by weight of catalyst in the catalyst-oil mixture. The size of the catalyst particles should be such that they provide the maximum surfaces consistent with economical recovery. It is desirable to employ catalysts containing a minimum of particles which are finer than 20 microns in order that the catalyst will readily separate with the residue and will not be carried off in the vapor stream and clog the fractionating equipment.

The mixture of oil and catalyst formed in slurry tank 6 is passed through line 8 and pumped by pump 9 and through line 10 into line 11 wherein it meets oil passed from tank 1 and pumped through line 12. We may also introduce through line 12c, controlled by valve 12b, olefinic hydrocarbons, such as butenes and pentenes, which may be converted into high knock-rating gasolines and may themselves be isomerized into isobutylene and isopentene and will increase the yield of iso compounds in the subsequently liquefied gases and also enhance the anti-knock rating of the gasoline formed in the process. The mixture passes through line 11 wherein it meets recirculated oil passing through line 13, as will be later described. The oil with the proper catalyst to oil ratio passes through the cracking coils 14 in furnace 15.

The exit temperatures employed in the cracking coil will vary from about 850 to 950° F., depending upon the cracking time provided in the cracking coils and the nature of the cracking stock employed and ratio of catalyst to cracking stock and desired degree of conversion. These temperatures may be compared with temperatures of about 1050° F. employed in suspensoid cracking. The pressure employed is that necessary to move the oil through the system, the exit coil pressure employed being from atmospheric to 300# per square inch. I regulate the cracking time by variation of oil throughput, the length of coil (or subsequent drum), and the discharge pressure from the coils to obtain the desired yield of gaso-

line, the desired gas formation and coke deposit. I may regulate the time and temperature of cracking to produce about 15 to 20% of aviation gasoline base stock of 300 to 325° F. end point or from 40 to 50% of 400° E. P. gasoline. These percentages are based on the charge to the cracking coils, being therefore "once through" values. In my process the cracking time permissible before excessive coke deposit and gas formation results is materially greater than that permissible in the higher temperature suspensoid cracking. The increased length of the cracking time permissible in my process results in the production of a gasoline having a materially higher anti-knock value and tetra-ethyl lead susceptibility than that produced by ordinary high temperature suspensoid practice.

The oil issuing from the cracking coil may be passed direct to the separator 17 by opening valves 15b and 16b, valves 15a and 16a being closed. Alternatively, a soaking drum 15 may be used to increase the cracking time of coil 14 and in such case the valves 15a and 16a are open and valves 15b and 16b are closed. Where the soaking drum is not employed, the converted oil, at the exit of the coil 14, is quenched with quenching oil passed through line 13a under control of valves 21a and 21b. The converted oil is reduced in temperature to below an active cracking temperature. The quench oil is introduced into the exit of the drum through line 13b by proper control of valve 13c with valve 21a closed.

When employing the soaking drum 15 the oil vapor and catalyst pass upward through the soaking drum, and the catalyst, through partial settling, tends to accumulate in the soaking drum, thereby increasing the catalyst to oil ratio. The cracked oil passes into a separator 17 in which the residual oil and catalyst separate from the vaporized material, and the oil-catalyst mixture discharges through the residuum outlet 18 through cooler 19 and is pumped by pump 20 through line 21 into surge tank 22 where it accumulates under pump pressure and passes through line 23 to filter 24. The filtrate passes through valved line 25 into accumulator tank 26 from which it is withdrawn by pump 27 to storage.

The vapors separated from the residue in 17 ascend through superimposed rectifying trays where they are fractionated by passage counter-current to descending reflux. As a result of the proper sizing of the catalyst there is substantially no carry-over of catalyst particles with the vapor from the tower.

The vapors withdrawn from the top of the separator-fractionator 17 pass through line 28 and are condensed in condenser 29 at a temperature sufficient to condense a heavy gas-oil fraction. The condensate is withdrawn through line 30 into surge drum 31 and passed through line 32 by pump 35. By control of the valve 33 a portion is recirculated through line 36 to act as a reflux in fractionator 17 and a portion is passed through line 13 to be used as dousing oil and cycle stock.

The uncondensed fraction issuing through line 37 enters the fractionating tower 38 in which it is refluxed to form heavy gas-oil bottoms. The bottoms are withdrawn through line 39 by pump 40 and passed through line 41 and joins the heavy gas-oil fraction by-passed through valve 33. The mixture passes through line 13 to be split at valves 21a and 21b, part passing to act as dousing oil through line 13a and part passing through line 13 to act as cycle stock.

At an intermediate point in tower 38, a light

gas-oil fraction is withdrawn through line 51 and passed by pump 52 to be employed as a wash oil in filter 24. The overhead from tower 38 passes through line 42 and condenser 43. The condensate there formed is collected in receiver 44 and the uncondensed gases vented through valved line 45. The condensate is passed through line 46 by means of pump 47 and by regulation of valves 48 and 49, part is introduced as a reflux over tower 38 through line 50 and part of the condensate is discharged through valved line 49 to storage as the gasoline-make of the plant.

The filter cake on filter 24 may be de-oiled by passing naphtha, benzol, acetone, phenol, or cresylic acid or other oil solvents through the filter cake to remove excess oil, or the cake may be discharged from the filter without preliminary de-oiling. We may employ the side cut withdrawn through line 51 as the de-oiling solvent. It is pumped by pump 52 through line 53 into the filter where it is used as a de-oiling wash on the filter cake. The wash liquid containing the extracted oil is removed through a separate connection 54 and passed by pump 55 through line 56 and introduced into tower 17. The un-deoiled or the de-oiled cake is discharged through suitable conveyors, schematically illustrated in line 70, and introduced in hopper 71 of a regenerating system.

I may employ as such regenerator a Herreshoff furnace or any other regenerator in which the clay is blown with a mixture of air and fuel gas in which the oxygen concentration is controlled to limit the temperature to which the catalyst is raised by the regenerative combustion to about 1000 to 1100° F. I prefer to employ a velocity of gases through the regenerator sufficient to levitate the portions of the catalyst finer than 20 microns and carry them off in the stream of gases issuing from the regenerator. The velocity of the gases should also be sufficient to remove the fine particles of iron oxide or other foreign materials which have contaminated the catalyst. By this procedure of regeneration and separation, I reform the catalyst to produce an active catalyst substantially free of carbon, iron oxide, or other contamination and produce an active catalyst of a particle size such that substantially none or but a minor amount of the material is less than 20 microns in size. I prefer to employ for this purpose a Herreshoff furnace. Such furnaces are well known and consist of a shaft in which there are superimposed shelves. The furnace has a central shaft, mounted so that it may be suitably rotated, and carries rabble arms which pass over the shelves and move the clay from shelf to shelf and across each of the shelves. Means are provided for introducing hot air whereby I may control the combustion of the coke on the catalyst and thus control the temperature to which the catalyst will be raised. The air velocity through the furnace is controlled by fans which introduce the air-fuel-gas mixture into the furnace. By controlling this velocity we are enabled to control the particle size and the amount of the clay withdrawn from the top of the furnace along with the exit gases. The gases issuing from the Herreshoff furnace will contain some material larger than 20 microns. The exit gases pass through flue 76 into a separator 77 in which the solid matter is selectively separated. For instance, this separator may be a cyclone or an electrical precipitator. In this separator the material of 20 microns or larger diameter is collected and discharged through line 78 to join the re-

generated material discharging through 73 and collected in bin 74. The material finer than 20 microns and the contaminating dusts are discharged with exit gases through 79.

It is to be understood that the foregoing description of the embodiments of my invention is for purposes of illustration, and modifications may be made therein without departing from the spirit of the appended claims.

I claim:

1. A process for catalytic cracking, which comprises, mixing oil with a fine-grained catalyst substantially free of particles of less than 20 microns in size, passing said mixture of oil and catalyst substantially free of particles of less than 20 microns in size through a coil positioned in a furnace, heating said mixture while passing through said coil to an active cracking temperature, separating said mixture into a vapor fraction and a liquid fraction containing said catalyst, removing the catalyst and the liquid fraction, separating the liquid fraction from said catalyst, introducing said catalyst into a regenerating furnace of the Herreshoff type, passing oxygen containing gases through said furnace to regenerate said catalyst, regulating the velocity of gases passing through said regenerating furnace to levitate the portions of the catalysts finer than 20 microns, discharging said gases carrying said catalyst particles from said regenerating furnace, removing from said regenerating furnace active catalyst substantially free of particles of less than 20 microns in size, and employing said last-named separated regenerated catalyst substantially free of particles of less than 20 microns in size to crack further oil in cycles of operation.

2. A method of catalytic cracking with powdered catalyst substantially free of particles of less than 20 microns in size, which comprises contacting a stream of oil with said catalyst substantially free of material of less than 20 microns in size recycled from a regenerating zone of a catalytic system, wherein said catalyst is broken down into particles of less than 20 microns in size, passing said catalyst countercurrent to a stream of regenerating gas containing oxygen to regenerate said catalyst, regulating the velocity of said stream to levitate the portions of the catalyst finer than 20 microns, discharging said gases carrying said catalyst fines from said regenerator, removing from the said regenerator a separate stream of catalyst substantially free of particles of less than 20 microns, and recycling said last-named catalyst to said oil in cycles of operation.

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