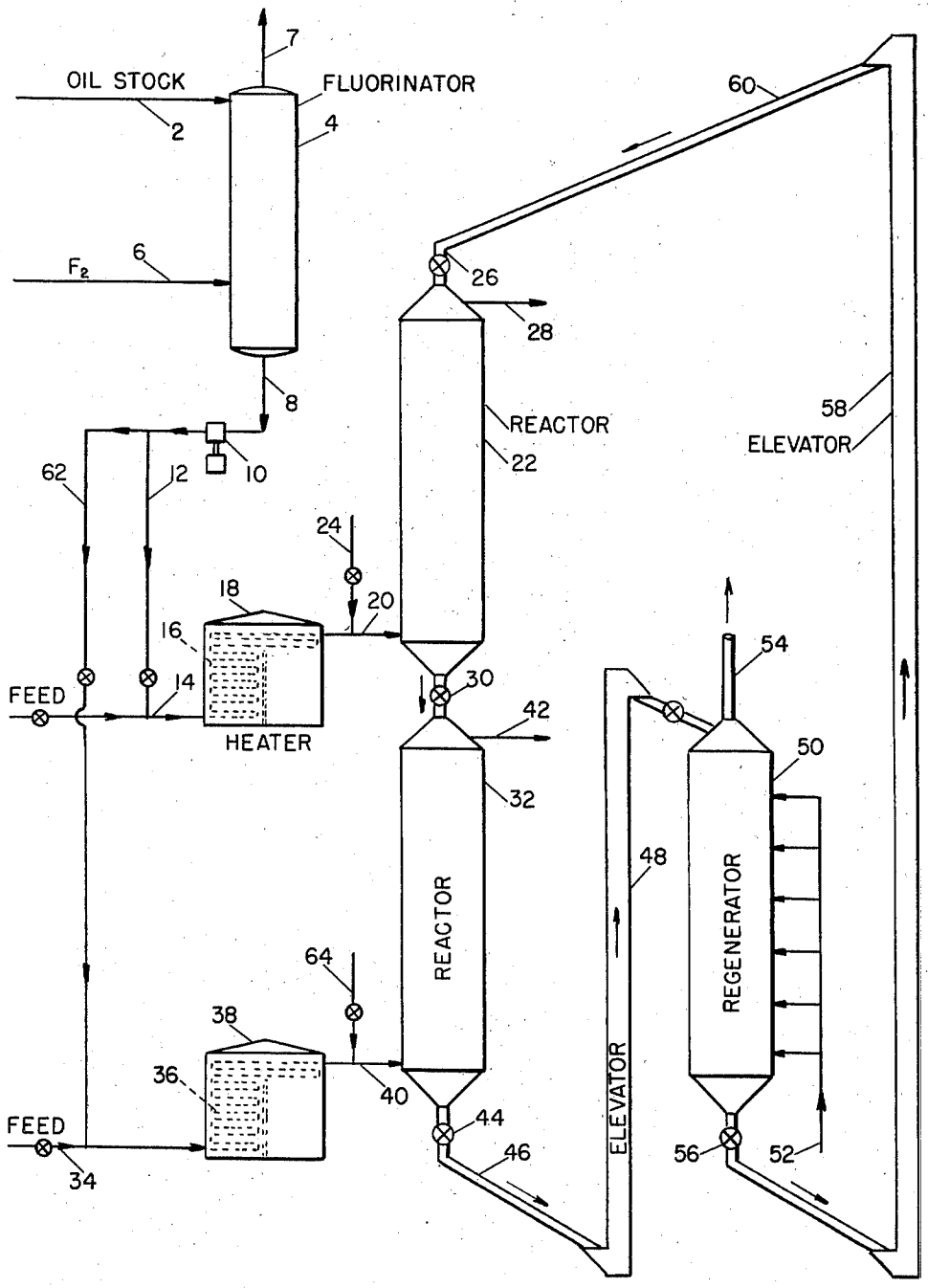
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CATALYTIC CONVERSION OF HYDROCARBONS

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CATALYTIC CONVERSION OF HYDROCARBONS

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This invention relates to the conversion of mineral oils for production of high anti-knock gasoline constituents, and more particularly to the cracking of prefluorinated feed stocks and recovery of the fluorine reaction products in the cracking operation.

When prefluorinated feed stocks are subjected to a cracking operation for the production of gasoline, the fluorine or fluoride is at least to a substantial extent converted to hydrofluoric acid which in all operations, as far as known, is not recovered in the cracking operation, but is permitted to go on through the fractionating equipment where it creates corrosion problems.

In accordance with the features of my invention, I obviate the difficulties previously encountered in such operations, and at the same time recover and make use of the hydrofluoric acid in a novel and effective manner. Therefore, an important feature of my invention is the contacting of the products of cracking of the prefluorinated feed stocks with conversion catalysts of the aluminum halide type, for the recovery of the valuable hydrofluoric acid and at the same time activate the aluminum halide catalyst.

Another feature of my invention includes the utilization of the activated aluminum halide catalyst in the conversion of hydrocarbon oil stocks. My improved process, therefore, may include a cycle in which the aluminum halide catalyst is used in a cracking operation and brought in contact with the products from the conversion of prefluorinated feed stocks either before or after regenerating the aluminum fluoride catalysts.

My improved process includes other features and advantages which are described in greater detail hereinafter in connection with the accompanying drawing which comprises a single figure in diagrammatic elevation illustrating an apparatus in which the combined operations of my process may be carried out.

As an illustrative example of my process, I take a gas oil charging stock and introduce it into the apparatus shown in the drawing, through a feed line 2, and pass it downwardly through a fluorinating unit 4 in which fluorine is introduced through a line 6. Suitable fluorinating conditions may be employed in the fluorinator 4, so as to fluorinate the gas oil stock with a suitable proportion of fluorine, for example, sufficient fluorine is introduced to fluorinate about, but not more than, one-tenth of the stock. The fluorine in the line 6 may be diluted with CO_2 or N_2. The reaction is effected at a temperature of from

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100° to 300° F., advantageously in contact with a copper reaction filter. Intercoolers may be provided in the unit 4 for controlling the temperature. Diluent gas is vented through a line 7.

The fluorinated stock produced in the unit 4 is withdrawn through a line 8 and placed under pressure by means of a pump 10, and passed through a valved line 12, into a valved charging line 14 leading to a cracking coil 16 in a pipe still furnace 18. The fluorinated stock is subjected to catalytic cracking in the coil 16 so as to produce suitable proportions of constituents boiling within the gasoline range. In this operation, the fluorine or fluoride content of the stock in acting to catalyze the cracking operation is itself largely converted to hydrofluoric acid.

The mixture of reaction products, including hydrofluoric acid, is conducted from the cracking zone in the coil 16 through a transfer line 20, into an enlarged chamber 22, which may be of the type used for a reactor in a moving bed catalytic operation. The stock in the transfer line 20 which may be at a temperature of from 900° to 1015° F. is preferably cooled to a somewhat lower temperature, as for example, from 800° to 850° F., by the introduction of a fluid cooling medium through a line 24. The cooling medium is preferably an anhydrous hydrocarbon or inert gaseous medium, but the reaction products are not cooled sufficiently to effect any condensation, since they are preferably kept in vapor phase in the chamber 22.

The reaction products, including hydrofluoric acid, introduced into the chamber 22 are brought in contact with an aluminum halide catalyst, as for example, aluminum fluorochloride ($AlFCl_2$), which is introduced into the chamber 22 through a valved supply duct 26. The aluminum halide catalyst is moved through the chamber 22 in a moving bed type of operation, and the catalyst may be in the form of freshly prepared extruded or bead catalyst with the aluminum halide deposited on or mixed with a carrier material such as alumina or silica-alumina compositions. The aluminum halide catalyst on the other hand may be a regenerated catalyst which has been used in a previous cracking operation.

The contact in chamber 22 effects a reaction between the hydrofluoric acid and the aluminum halide catalyst so as to recover the acid as a part of the aluminum halide catalyst and to activate the latter for use in a conversion operation. The reaction products from the cracking of the prefluorinated stock in the coil 16 are discharged from the upper portion of the chamber

22 through a vapor line 28 and sent to conventional fractionating and recovery equipment.

The operation carried out in chamber 22 may be conducted at a somewhat lower temperature than that given above, and one in which the products in the line 20 are introduced into the top of the chamber in a cooled condition, and withdrawn from the bottom of the chamber, partly in liquid form. In such a case, suitable means are provided for stripping the catalyst in the bottom of the chamber to free it of oil products.

The aluminum halide catalyst reacted with the hydrogen fluoride in the chamber 22 moves through a rotary feed valve 30 into a moving bed reactor 32 in which another catalytic cracking operation is carried out on an oil charging stock supplied through a valved line 34, heated to a cracking temperature of from 850° to 1000° F., in a coil 36 of a pipe still furnace 38, and discharged through a transfer line 40 in vaporized condition into the reactor 32 where the oil stock is catalytically converted in contact with the activated aluminum halide catalyst. The vapors produced in the conversion operation carried out in the reactor 32 are discharged therefrom through a vapor line 42, and sent to conventional fractionating and product recovery equipment.

Spent aluminum halide catalyst reaching the bottom of the reactor 32 is discharged therefrom through a rotary feed valve 44 and passed through a chute 46 into an elevator 48 from which the spent catalyst is supplied to a regenerator 50 through suitable connections, as shown. The catalyst moves through the regenerator 50 in a moving bed operation and is regenerated by the introduction of air and other suitable dry gases through the line 52 and other necessary lines conventionally employed in such regenerating operations, the spent gases being discharged through a duct 54.

The regenerated catalyst is discharged from the regenerator 50 through a rotary feed valve 56 and supplied to an elevator 58 which elevates the catalyst to a supply duct 60 for the chamber 22.

Any of the known aluminum halide cracking catalysts may be used, such as the one referred to above, and AlF_2Cl, $AlCl_3$, AlF_3, and others. The reaction between these catalysts and the hydrofluoric acid in the chamber 22, or in the chamber 32, as described hereinafter, may produce complex aluminum halides in addition to being activated by the hydrofluoric acid. Some of these compositions may comprise aluminum halides in which HF is combined therewith. All operations are essentially anhydrous or such that not more than about one-half mol of water is present per mol of halide catalyst.

In the foregoing illustration of the improved process, the operation includes the step of contacting the reaction products from the cracking of the prefluorinated stock with a fresh or revivified aluminum halide catalyst, in the chamber 22. Substantially the same apparatus may be used for contacting the reaction products containing the hydrofluoric acid with the spent catalyst from a cracking operation wherein aluminum halide catalysts are employed. In such an operation, the prefluorinated charging stock supplied by the pump 10 is conducted through a valved line 62 instead of the line 12, and introduced into the valved line 34 in place of the charging stock previously supplied thereto. The cracking of the prefluorinated stock is therefore effected in the pipe still heater 38, the resulting products cooled by the introduction of a cooling medium through

a valved line 64, and the resulting product mixture discharged through the vapor line 40 into the reactor 32 where it is contacted with spent aluminum halide catalyst from the chamber 22. In such an operation, a gas oil or other charging stock to be cracked catalytically by contact with fresh or revivified aluminum halide catalyst, is supplied through the valved line 14 to the pipe still 18 and cracked in the chamber 22 which is used in this instance as a reactor. The aluminum halide catalyst is supplied to the chamber 22 through the duct 26.

The type of operation, therefore, outlined immediately above, involves the catalytic conversion of an oil charging stock with an aluminum halide catalyst in the reactor 22, the catalyst being either fresh catalyst or revivified catalyst, while the spent catalyst passes to the chamber 32, which in this instance, is not used as a reactor except to activate the aluminum halide catalyst and recover hydrogen fluoride from the prefluorinated stock cracked in the pipe still furnace 38. The spent aluminum halide catalyst is used to accomplish this result prior to being revivified in the chamber 50.

Various stocks such as gas oils, naphthas and others may be converted by cracking, alkylation, hydroforming, isomerization or other forms of conversion.

I claim:

1. The improvement in the cracking of hydrocarbon oils for the production of high anti-knock gasoline, which comprises cracking a prefluorinated oil stock in a cracking zone at a cracking temperature and thereby producing gasoline range constituents and hydrofluoric acid, contacting the cracked products including the hydrofluoric acid with an aluminum halide catalyst to recover in the form of a product of reaction between hydrofluoric acid and the aluminum halide catalyst the hydrofluoric acid from the products of said cracking, passing the aluminum halide catalyst including the product of the reaction between said aluminum halide catalyst and the recovered hydrofluoric acid into a separate cracking zone and therein catalytically cracking a different hydrocarbon oil charging stock.

2. The process as defined by claim 1 in which the spent aluminum halide catalyst from the aluminum halide cracking zone is revivified and thereafter recycled for contact with the reaction products including hydrofluoric acid from the cracking of the prefluorinated oil stock.

3. The improvement in the conversion of hydrocarbon oils for the production of high anti-knock gasoline, which comprises converting a hydrocarbon oil stock by passing it at a conversion temperature in intimate contact with an aluminum halide catalyst in a reaction zone, supplying an aluminum halide catalyst to the reaction zone, removing the spent aluminum halide catalyst from said zone into a separate contact zone, catalytically converting a prefluorinated oil stock in a second conversion zone at a conversion temperature, and passing the resulting reaction products including hydrofluoric acid from the last-mentioned zone into the contact zone in intimate contact with the spent aluminum halide catalyst, thereby recovering the hydrogen fluoride in the form of a product of reaction between the hydrogen fluoride and the aluminum halide catalyst.

4. The process defined by claim 3 in which the reaction products from the conversion of the prefluorinated stock are cooled prior to bringing

them into contact with the spent aluminum halide catalyst.

5. The process defined by claim 3 in which the aluminum halide catalyst is removed from the contact zone, revivified, and the resulting revivified catalyst supplied to the first-mentioned conversion zone.

6. The improvement in the conversion of hydrocarbon oils for the production of high anti-knock gasoline, which comprises cracking a hydrocarbon oil at a cracking temperature in contact with an aluminum halide catalyst in a reaction zone, circulating the aluminum halide catalyst through the zone, through a regenerating zone and then back to the reaction zone, fluorinating an oil charging stock and subjecting it to cracking conditions in a separate cracking zone, contacting the products from the cracking of the fluorinated oil stock with the aluminum halide catalyst at a point in its cycle outside the aluminum halide

cracking zone thereby utilizing the aluminum halide catalyst for recovering, in the form of a product of reaction between hydrofluoric acid and and the aluminum halide catalyst, the hydrofluoric acid content of the products from the cracking of the fluorinated feed stock and for activating the aluminum halide catalyst.

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