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MANUFACTURE OF LIQUID HYDROCARBONS

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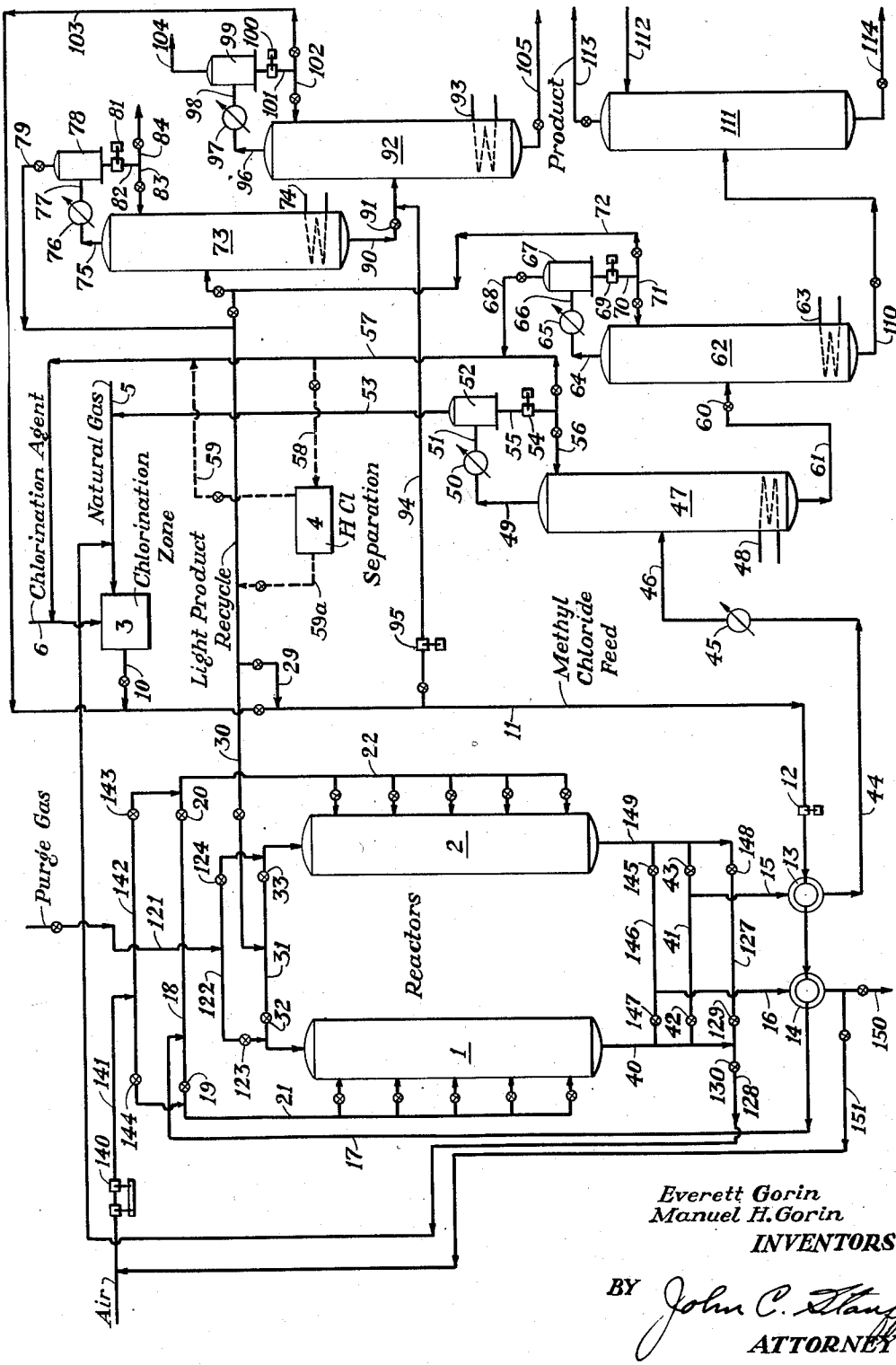

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MANUFACTURE OF LIQUID HYDROCARBONS

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6 Claims. (Cl. 260—677)

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This invention relates to the conversion of normally gaseous hydrocarbons to hydrocarbons of higher molecular weight. More particularly, this invention relates to the conversion of methane and natural gas to a mixture of normally liquid hydrocarbons in a unitary process wherein the normally gaseous hydrocarbons are converted to the corresponding alkyl halides which are then condensed in a dehydrohalogeno-condensation reaction. The particular feature of the present invention is the recycle of at least a part of the normally gaseous primary condensation products for use as diluent of the alkyl chlorides in the condensation reaction. The term normally gaseous primary condensation products as used in the specification and claims refers to the C_2, C_3, and C_4 hydrocarbons formed in the condensation process.

It is known to condense light alkyl halides by pyrolysis in strictly thermal conversions. For example, in the patent obtained by one of the present inventors, U. S. 2,320,274, entitled Conversion of normally gaseous hydrocarbons, it is taught to halogenate the hydrocarbons and then pyrolyze the light alkyl halides at temperatures above about 500° C. to produce benzene, acetylene, and ethylene. The method requires relatively high temperatures in the pyrolysis step. Where it is desired to produce normally liquid hydrocarbons by the condensation of the alkyl halides such as methyl chloride and ethyl chloride lower temperatures are highly desirable.

It, therefore, is an object of our invention to provide an improved process for converting normally gaseous hydrocarbons such as methane and ethane to normally liquid hydrocarbons. Another object is to produce from methane and natural gas, hydrocarbons and hydrocarbon derivatives of higher molecular weight, at least a part of which is utilizable in the form of recycle to the condensation reaction zone. A more specific object is to provide a process for condensing methane at temperatures below 500° C. to normally liquid hydrocarbons by halogenation of the methane, and condensing the methyl halide in the presence of recycled primary condensation products. These and other objects will be apparent from the description of our invention.

Methane is available in enormous quantities in natural gases. Natural gases are composed primarily of methane and ethane and usually contain progressively smaller amounts of propane, butane, pentane and higher hydrocarbons. Natural gases which contain the higher molecular weight hydrocarbons are usually termed wet gases. After the removal of the condensible components, which may be used as such as motor fuel blending agents or which may be processed by dehydrogenation and/or isomerization to produce alkylation feed stock for the production of

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aviation blending naphthas, the residual non-condensible light hydrocarbons consisting of methane, ethane, and a small amount of propane are generally useful only as fuel. Hence, artificially "dried" natural gas as well as naturally occurring dry gas containing methane, ethane, and a small amount of propane may be used in our process.

We have found that the difficulties of prior art processes may be eliminated by employing a two-step operation wherein the light hydrocarbon such as methane or ethane or mixture of these is converted to a more reactive compound, and then this more reactive compound or mixture of compounds is catalytically treated to condense the hydrocarbon radicals of two or more of the more reactive intermediates. Thus, for example, we have found that if methane is first converted to a methyl halide, the methyl halide may be catalytically condensed to hydrocarbons having two or more carbon atoms to the molecule. The corresponding hydrogen halide is eliminated from the methyl halide and may be reused for the production of methyl halide as described in the copending application of E. Gorin, entitled Hydrocarbon conversion process, Serial No. 507,618, filed October 25, 1943, now U. S. Patent 2,407,828, and also described in the copending joint application of C. M. Fontana and E. Gorin, entitled Manufacture of halogenated hydrocarbons, Serial No. 548,351, filed August 7, 1944. The first step of our process, namely, the halogenation of the paraffin hydrocarbons, may be carried out by other methods well known to those versed in the art.

The dehydrohalogeno-condensation of methyl chloride is effected by the aid of catalysts which possess both dehydrohalogenation and polymerization activity. Suitable catalysts are those which comprise an association of amphoteric and acidic oxides such as alumina on silica, zinc oxide on silica, boric oxide on alumina, beryllium oxide on silica or gallium oxide on silica. Other mixed oxide catalysts such as magnesia-silica, zirconia-silica, or thoria-silica may be used. Pure amphoteric or acidic oxides may be used alone, such as, for example, alumina, silica, or titania. Active catalysts may also be prepared from naturally occurring materials such as by acid-treating clays of the fuller's earth, bentonite, montmorillonite, or Attapulgus variety. Strictly acid-type catalysts such as phosphoric acid or pyrophosphoric acid, preferably mounted on a carrier such as kieselguhr, may also be used. However, we prefer to use the mixed oxide-type catalyst containing two or more oxides, particularly the activated alumina-silica catalyst.

The oxide catalysts are generally prepared in such a way that they are subjected to an acid environment in the last stages of their preparation in order that traces of alkali metal oxides

which act as catalyst poisons be substantially completely removed. However, when the only cation present during the preparation of the catalyst is the cation of a volatile base such as ammonia, this purification may be omitted. Alumina or alumina-silica catalysts containing more than traces of sodium are relatively inactive toward the dehydrohalogenation of methyl chloride. However, when the sodium is removed by treatment with dilute acid or by salts of weak bases such as ammonium chloride, aluminum chloride, or aluminum sulfate followed by water washing, drying, and calcining at about 500° C. these catalysts become highly active. Gel-type catalysts having high porosity are preferred, and it is highly desirable that the catalyst be capable of withstanding high temperatures such as those produced by oxidative regeneration, since considerable carbon is deposited on the catalyst in the reaction cycle which must be removed in order to restore the catalyst activity. Our preferred alumina gel and silica gel or combined alumina-silica catalysts possess the above-desired properties.

The alumina gel is preferably prepared by forming an alumina sol. A mercury-aluminum amalgam is digested in a dilute acid such as acetic acid. The clear sol is separated from the unreacted amalgam and after setting to a gel the alumina gel is separated. Setting of the gel may be promoted by evaporation at 50° C. to 100° C. or by precipitation with dilute ammonia. Silica hydrogel may be prepared by addition of sodium silicate solution to an excess of mineral acid such as sulfuric acid. To prevent precipitation of the silica violent agitation and cooling of the acid may be used. These precautions may be omitted if acetic acid is used instead of mineral acid in which case the buffering action of the sodium acetate formed prevents precipitation of the silica. The moist washed gels of alumina and silica are ballmilled together, dried at 100° C., and activated by heating at about 500° C. for several hours to form the finished alumina-silica gel catalyst. The mol ratio of alumina to silica may be varied over a wide range since each of the pure gels taken separately are catalysts for the dehydrohalogeno-condensation reaction. It is generally preferred, however, to employ a considerable excess of silica gel over alumina gel and more particularly a mol ratio of about thirty to one to about five to one is preferred.

Other methods may be employed to combine the alumina and the silica. Thus, alumina may be deposited on the silica gel by hydrolytic precipitation of alumina from a dilute solution of an aluminum salt; that is, alumina may be precipitated on the silica gel by digestion of a suspension of the gel in an aluminum salt solution. The alumina, on the other hand, may be precipitated on the silica by the addition of a basic reagent such as ammonia or ammonium carbonate to a suspension of silica gel in an aqueous solution of an aluminum salt. The mixed oxides of silica and alumina may be prepared as co-gels by mixing solutions of sodium aluminate and sodium silicate and allowing the mixture to set to a clear hydrogel which is then broken to a relatively small particle size, thoroughly washed and treated with dilute acid to remove sodium therefrom, dried and activated by heating as described above.

The above catalysts are comparatively inactive at temperatures below 250° C. while in most cases

temperatures above 300° C. are required to effect a reasonably rapid reaction. Temperatures in excess of about 500° C. are unsuitable due to excessive decomposition of the products. Our preferred temperature range for operating the dehydrohalogeno-condensation reaction is from about 350° C. to about 425° C. A wide range of pressures may be employed in carrying out the conversion of alkyl chlorides to hydrocarbons having a greater number of carbon atoms, such pressures varying from one atmosphere to about forty atmospheres or higher.

The pressure employed in our process has a decided effect on the nature and distribution of the products. For example, when the process is carried out at high temperatures and low pressures with methyl chloride feed, the gaseous fraction consists primarily of low molecular weight olefins such as ethylene, propylene, and butylene, and the gasoline fraction contains considerable unsaturates. When higher pressures, i. e., above six or seven atmospheres and temperatures below 400° C. are employed, the gaseous fraction contains relatively larger amounts of saturates than unsaturates, and the gasoline fraction is almost completely saturated. Under the latter conditions the lower boiling fraction of the liquid product is highly branched and contains large amounts of such components as isopentane, 2,3-dimethyl butane and 2-methyl pentane and, hence, may be used as a blending stock for aviation gasoline. The heavier fractions are rich in aromatic hydrocarbons. Relatively large amounts of isobutane are formed under low temperature-high pressure operation while the lighter gases consist of a mixture of ethylene, propylene, ethane, and propane. In addition, ethyl chloride is usually produced, the ratio of ethyl chloride to ethylene being higher in the case of low temperature-high pressure operation. We prefer to operate at pressures within the range of from about 15 to about 40 atmospheres. In general, only traces of alkyl chlorides boiling above ethyl chloride are produced when methyl chloride and ethyl chloride are condensed under the above conditions.

The optimum space velocity for carrying out the dehydrohalogeno-condensation of alkyl halides depends on the particular alkyl halide, on the catalyst, and on the temperature and pressure employed. For methyl chloride the space velocity expressed in terms of volumes of methyl chloride gas at standard temperature and pressure passed per volume of catalyst per minute is in general higher the higher the temperature and the higher the pressure, and for our preferred alumina-silica gel catalyst lies within the range of from about 5 to about 50 volumes of gaseous methyl chloride per volume of catalyst space per minute at temperatures within the range of 350° C. to 425° C. and pressures from one atmosphere to twenty atmospheres. When operating at pressures of from about twenty atmospheres to about forty atmospheres within the temperature range of 370°–400° C. with the alumina gel-silica gel catalyst, we prefer space velocities within the range of from about 5 to 20 volumes of gaseous methyl chloride per volume of catalyst space per minute.

The light olefins such as ethylene, propylene, and butylene produced in the reaction may be recycled for conversion to liquid hydrocarbons by polymerization and condensation with the methyl chloride. It is also advantageous to recycle the isobutane and ethyl chloride produced

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since these materials are likewise converted to liquid hydrocarbons by condensation with the methyl chloride or with primary products such as ethylene formed from the methyl chloride. We have found that higher yields of the liquid hydrocarbons are obtained when the condensation of methyl chloride is carried out in the presence of active diluents such as ethylene, propylene, isobutane, and ethyl chloride which are reacted to form hydrocarbons of four or more carbon atoms. Inactive diluents such as propane and normal butane likewise have a favorable effect on the reaction due to their dilution effect resulting in keeping the instantaneous concentration of methyl chloride at a low figure which is desirable for the most successful operation of our process. We also maintain a low instantaneous concentration of methyl chloride by introducing the vaporized feed at a multiplicity of points to the stationary catalyst bed described in our preferred method of operation below.

Referring now to the drawing, towers 1 and 2 contain alumina gel-silica gel catalyst either as a continuous bed or disposed in trays. We prefer the latter method of packing these towers, since the difficulty of controlling regeneration temperatures is reduced if the catalyst is maintained in a series of relatively shallow beds. Towers 1 and 2 are manifolded in such a manner that while one of these is on stream for the condensation reaction the other is undergoing oxidation regeneration thus providing for substantially continuous operation. The hydrocarbon halogenation zone is represented diagrammatically by 3. As indicated hereinabove, dry natural gas containing methane and ethane is introduced to zone 3 through line 5. Chlorine or hydrogen chloride and oxygen are introduced to the chlorination zone through line 6. Zone 4 is provided for the separation of hydrogen chloride from C_2 hydrocarbons in the product.

Liquid methyl chloride is passed from zone 3 through valved line 10 and line 11, and is discharged at a pressure of from about 500 to about 600 pounds per square inch by means of pump 12, whence it is passed through heat exchangers 13 and 14 for absorbing heat from the reaction product in line 15 and hot regeneration gases in line 16. From exchanger 14 the hot feed product passes via line 17 to manifold line 18 provided with valves 19 and 20 and connected with reactor feed manifold lines 21 and 22. With valve 19 in line 18 open and valve 20 closed, the hot methyl chloride vapor is introduced to tower 1 by a multiplicity of valved feed lines leading from manifold line 21 at a temperature within the range of 370° C.–400° C. and a space velocity within the range of 5 to 20 volumes of methyl chloride per volume of catalyst space per minute.

We have found that both inactive and reactive diluents aid in the condensation of methyl chloride and hence, we introduce isobutane and ethyl chloride product from the primary condensation through line 30 which joins manifold line 31 provided with valve 32, which is open for transfer of diluent, and valve 33 which is closed. Where it is desirable to eliminate excess propane and normal butane from the process, isobutane diluent from the product may be furnished in the form of methyl chloride-isobutane azeotrope, as described hereinbelow, via recycle line 103 which connects with feed line 11. The mol ratio of hydrocarbon diluent recycle stock to total alkyl chloride fed to reactor 1 may be from about 0.5 to 1 to about 3 to 1 while the internal ratio of

diluent to alkyl chloride is preferably maintained within the range of from about 4 to 1 to about 10 to 1 or higher. Under this mode of operation from 50 to about 90 per cent of the alkyl chloride is decomposed per pass and from 80 to 85 per cent of the alkyl chloride decomposed forms hydrocarbons having a greater number of carbon atoms than the alkyl chlorides in the feed to the reactor, 15 to 20 per cent appearing as carbon and methane decomposition products. The use of diluents, either active or inactive in the condensation reaction, reduces greatly the amount of carbon and methane formation, thereby directing the condensation reaction toward the formation of the more valuable liquid hydrocarbon product.

In our process the diluents are supplied exclusively from the normally gaseous hydrocarbons produced in the product, which hydrocarbons are characterized by having more than one carbon atom and less than five carbon atoms per molecule. We also recycle unreacted alkyl chloride reactants. The inactive diluents such as ethane, propane, and normal butane are usually recycled only in part. Since the separation of a mixture of ethylene and ethane from hydrogen chloride is difficult and since the mixture of these gaseous components of the product may be used advantageously to produce alkyl chloride feed to the condensation reaction, the ethane and ethylene are recycled only in part to the condensation reaction zone. Thus, we prefer to recycle a part of the ethylene and substantially all of the propylene and isobutane, and to withdraw from the recycle stream excess propane and normal butane which tend to build up in the system. At least a part of these paraffinic hydrocarbons may be returned to the reaction zone to maintain in the feed thereto a ratio of hydrocarbons to alkyl chlorides within the range of from 0.5 to 1.0 to 3.0 to 1.0.

The product from reactor 1 consisting of a mixture of methane, hydrogen chloride, ethylene, ethane, ethyl chloride, propane, propylene, unreacted methyl chloride, isobutane and other C_4 hydrocarbons along with higher boiling hydrocarbons is passed by drawoff line 40 to manifold product line 41 which is equipped with valves 42 and 43, the latter being closed and the former open for delivery of the product to line 15 leading to heat exchanger 13 where the product is subjected to initial cooling. From exchanger 13 the product passes via line 44 to cooler 45 and thence by line 46 to fractionator 47. Fractionator 47 which is provided with indirect heating means 48 operates as a stripping column for the removal of light gases from the reaction product, the pressure maintained therein being somewhat lower than the pressure in reactor 1. These light gases comprising methane, ethylene, ethane, and a part of the hydrogen chloride product of the reaction pass overhead through line 49 to condenser 50 and thence by line 51 to reflux drum 52. Overhead gas consisting primarily of methane is recycled through valved line 53 to line 5 and thence to the methane chlorination process for the production of methyl chloride feed to the process. Condensate in reflux drum 52 is removed therefrom by pump 54 in line 55 to be returned in part to tower 47 as reflux through valved line 56, a part of excess condensate being sent via valved line 57 and line 6 to the methane chlorination process described in the aforementioned copending application, Serial No. 548,351, or to other

hydrogen chloride recovery systems. If desired, a part of the stream in line 57 which contains the C_2 hydrocarbons and hydrogen chloride may be passed to zone 4 through line 58 where hydrogen chloride is separated from these gases by any means well known in the art, such as, by absorption. The hydrogen chloride is recycled to chlorination zone 3 via lines 59, 57, and 6, and the C_2 hydrocarbons are recycled to the condensation zone as diluent through lines 59a, 30, and 31. It has been found that large amounts of hydrogen chloride have an inhibiting effect on the course of the condensation reaction, and it is usually desirable to maintain the hydrogen chloride concentration below 25 per cent of the total gas and in any case hydrogen chloride should not constitute over 50 mol per cent of the total gas effluent from reactor 1. Hence, hydrogen chloride is removed as far as practicable from recycle stock in order to hold the concentration of hydrogen chloride in reactor 1 to a minimum.

The liquid product from fractionator 47 is transferred via pressure release valve 60 in line 61 to butanizer tower 62 for the removal of propane, propylene, the C_4 fraction, unconverted methyl chloride and ethyl chloride from the higher boiling product. These products are all suitable for recycle, at least in part, to reactor 1 either as diluents to promote the reaction or as condensable alkyl chlorides. The overhead from tower 62 will also contain hydrogen chloride in minor amounts which is retained in the bottom product from tower 47 as a result of the relatively high pressure fractionation in tower 47. Tower 62 is operated at a pressure of about 200 pounds per square inch and is provided with reboiler means 63. The overhead gaseous product from tower 62 passes via line 64, condenser 65, and line 66 to reflux drum 67 from which noncondensed gas, primarily hydrogen chloride passes via valved line 68 to line 57 for use in producing methyl chloride as described in the afore-mentioned copending applications. Condensate from reflux drum 67 is picked up by pump 69 in line 70, a part being transferred through valved line 71 to tower 62 as reflux and the remainder passed via valved line 72 to recycle line 30. As stated hereinabove, the components of the stream in line 72 are all suitable for recycle to the reaction zone. Hence, valved recycle line 30 is provided, which leads from line 72 directly to manifold line 31. If desired, this recycle product may be diverted to the main feed stream in line 11 via valved line 29 leading from line 30. The C_3 and C_4 hydrocarbons, ethyl chloride, and, if desired, a part of the C_2 hydrocarbons are recycled as described above until the concentration of diluent in condensation tower 1 is built up to the hereinabove described ratio of diluent to virgin and recycle alkyl chloride. Excess diluent such as propane and normal butane produced in the process are eliminated therefrom as described hereinbelow.

When the propane and/or normal butane content of the stream in line 72 becomes excessive, a part of said recycle stream is diverted to tower 73 to separate propane and propylene from the C_4 hydrocarbons and alkyl chlorides. Tower 73 is maintained at a pressure of from about 200 to 250 pounds per square inch with tower top temperature maintained at about 35° C. to 40° C., tower 73 being provided with reboiler means 74. The overhead consisting of propylene and propane passes via line 75, cooler 76 and line 77 to reflux drum 78. Uncondensed propylene passes via line 79 to recycle line 30 and the condensate is removed from drum 78 by means of pump 81 in line 82 for transfer in part to tower 73 as reflux via valved line 83 and the remainder, comprising relatively pure propane, may be sent to storage via line 84. When it is desired to increase the ratio of propane diluent to normal butane in reactor 1 a part of propane in line 84 is introduced to line 30 and recycled to the condensation reaction.

The bottom product from tower 73 is transferred via line 90 and pressure release valve 91 to deisobutanizer tower 92 which is provided with reboiler means 93 and which is operated at pressures within the range of 100 to 150 pounds per square inch. We have found that methyl chloride forms an azeotrope with isobutane and hence the overhead from tower 92 consists primarily of methyl chloride-isobutane azeotrope boiling at about −25.6° at atmospheric pressure, provided these components are present in the proper proportions. This azeotrope consists of approximately 77 mol per cent methyl chloride and 23 mol per cent isobutane. Provision is made for adding methyl chloride to line 90 via valved leadoff line 94 from line 11 by means of pump 95 for augmentation of methyl chloride to tower 92 when the conversion in reactor 1 is sufficiently high that there is insufficient methyl chloride to form the desired azeotrope with isobutane. Where it is undesirable to recycle all of the isobutane the excess isobutane not combined as the azeotrope may be removed along with normal butane through line 105 described below. The separation of isobutane from the other C_4 hydrocarbons and ethyl chloride is sharp. Hence, the overhead product from tower 92 will contain only a trace of propane and the azeotrope plus any of the uncombined components of the azeotrope mixture, that is, free isobutane or free methyl chloride. The overhead passes through line 96, condenser 97, and line 98 to reflux drum 99 whence the condensate is sent in part by means of pump 100 in line 101 and via valved line 102 to tower 92 as reflux, the remainder being passed via valved line 103 for recycle through line 11 to reactor 1 as described hereinabove. Any accumulation of gaseous propane in drum 99 is removed via line 104 to storage. The C_4 bottom fraction which is removed from tower 92 via line 105 contains some ethyl chloride which may be separated by scrubbing with an alcohol-water mixture and the separated ethyl chloride may be recycled to reactor 1 while the C_4 fraction may be subjected to alkylation and/or isomerization reactions to produce aviation grade gasoline. If desired, a part of the C_4 bottom fraction from tower 92 may be recycled to reactor 1 in order to maintain the desired ratio of hydrocarbon to alkyl chloride in the feed as described hereinabove.

Returning now to debutanizer tower 62, the bottom product consisting of C_5 and higher boiling hydrocarbons is withdrawn via line 110 leading to wash tower 111 where it is washed countercurrently with an aqueous caustic solution introduced to tower 111 through line 112 to remove any traces of hydrogen chloride. The C_5+naphtha passes overhead to storage through line 113 and the partially spent caustic wash is withdrawn via valved line 114 for suitable disposal.

After reactor 1 has been on stream for an interval up to 90 minutes depending on the operating conditions relative to space velocity and pressure, sufficient carbon will have accumulat-

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ed on the catalyst to necessitate reactivation. This is accomplished by passing air through the reactor, the air being diluted with flue gas in order to control the rate of oxidation and to maintain the regeneration temperature below about 650° C., preferably below about 600° C. However, reactor 1 and the catalyst therein will contain some hydrogen chloride and other reaction products which may be recovered by purging the reactor prior to oxidative reactivation. It is desirable to remove the hydrogen chloride and the residual hydrocarbons prior to burning the carbon from the catalyst since the combustion of the hydrocarbons results in the formation of water vapor and the presence of water vapor with hydrogen chloride aggravates corrosion problems.

Tower 1 is isolated for purging before regeneration by opening valve 130 in line 128, and closing valve 124 in line 122, valve 32 in line 31, valve 144 in line 142, valve 147 in line 146, valve 42 in line 41, and valve 129 in line 127. Methane purge gas is introduced via line 121 and passes via lines 122 and 31 to reactor 1 for removal of residual hydrogen chloride and hydrocarbon vapors. The purge gas leaves reactor 1 through line 40 and thence passes via line 128 to line 5 for transfer to the methyl chloride production zone 4. The methane purging operation is followed by a short flue gas purge in order to clear reactor 1 of methane prior to the reactivation step.

Referring now to the reactivation operation which is carried out in tower 2 while reactor 1 is on stream for the condensation reaction and for the purging operation, a mixture of air and flue gas is introduced to the system by means of compressor 140 in line 141. The extent of dilution of oxygen in the regenerating gas should be such that temperatures in excess of 650° C. are avoided and preferably the temperature should not exceed 600° C. since synthetic alumina-silica catalyst and also acid-treated clays tend to become permanently deactivated at higher temperatures. Control of reactivation temperatures is more readily obtained by disposing the catalyst in a series of relatively shallow beds rather than as a continuous bed. The flue gas diluted air is passed from line 141 to manifold line 142, which is provided with valves 143 and 144, and thence to line 22 for introduction to tower 2 via manifold and valved feed lines leading from line 22. The regeneration zone is isolated by closing valve 144 in line 142, valve 20 in line 18, valve 147 in line 146, valve 43 in line 41, and valve 148 in line 127, and provision for continuous flow of regeneration gas is made by maintaining valve 143 in line 142 and valve 145 in line 146 in the open position. The regeneration gas passes from tower 2 via line 149 and is passed via lines 146 and 16 to heat exchanger 14, whence it is eliminated from the system through valved line 150. If desired, a part of the spent regeneration gas may be recycled to line 141 through valved line 151 for dilution of fresh regeneration air. The flow of regeneration gas is continued for a temperature adjustment period following complete reactivation of the catalyst until the catalyst bed temperature has lowered to such a level that fresh feed will be held within the desired temperature range for the condensation reaction. The purge gas should contain no oxygen during this purging operation.

Although we have described our invention as being carried out at pressures in excess of 300 pounds per square inch and preferably at pressures of about 500 pounds per square inch, we do not wish to be limited to this type operation. The dehydrohalogeno-condensation reaction may be carried out at pressures below 300 pounds, for example, of the order of atmospheric to 50 pounds per square inch. However, such type operation involves greater expenditure of capital for compression equipment for separation of predominantly gaseous hydrocarbon product when operating at low pressures and higher temperatures. Certain advantages favor low pressure operation. For example, the carbon deposited on the catalyst may be removed more advantageously by operating the oxidative reactivation step by the well-known hindered flow-type procedure which is usually adaptable at pressures below 75 or 100 pounds per square inch. In this type of operation the catalyst is in the form of powder which is introduced to the regeneration zone suspended in the regeneration gas and maintained therein by regulating the flow of gas through the regeneration zone at such a velocity that the fluidized powder assumes physical properties not unlike those of a boiling liquid. Oxidative regeneration temperatures are more uniform and more easily controlled in such type operation. This type operation may also be applied to the dehydrohalogeno-condensation side of the process if the pressure is maintained below 75 or 100 pounds per square inch.

We may also adopt other methods of catalytic contacting to our process of converting methyl chloride to normally liquid hydrocarbons. For example, the various types of moving catalyst bed techniques well known in the art of hydrocarbon conversion, particularly in the art of converting petroleum hydrocarbons and hydrocarbon mixtures, may be used if relatively low pressure operation is followed.

The following examples are introduced to show the effects of pressure and diluents in carrying out our process. Separately prepared moist silica gel and alumina gel were ball-milled in a mol ratio of silica gel to alumina gel of approximately 8 to 1, the mixture was dried at a temperature below 100° C. and finally activated by calcining at 500° C. for about 20 hours. This catalyst was used in obtaining the following results.

Example 1

Methyl chloride was passed over a sample of the above alumina-silica gel catalyst at 425° C. and at a space velocity of 4.3 volumes of methyl chloride vapor per volume of catalyst space per minute, the reaction zone being maintained at atmospheric pressure. 24.5 per cent of the methyl chloride was decomposed to give a product which analyzed as follows:

Product	Mols Carbon/100 mols CH_3Cl decomposed
CH_4	19.1
C_2H_4	8.6
C_3H_6	4.8
C_4	18.7
C_5	5.1
C_6	3.0
C_7+	2.0
Carbon	38.7
	100.0

The C_3 and C_4 fractions were completely unsaturated and liquid fractions boiling above the C_4 fraction contained a high proportion of unsaturates. Only ten and one-tenth mols of carbon per hundred mols of methyl chloride decomposed

were accounted for in hydrocarbon product boiling above the C_4 fraction, that is, in the normally liquid hydrocarbon fraction.

Example 2

Methyl chloride was passed over a sample of the above alumina-silica gel catalyst at 300 pounds per square inch pressure at a space velocity of approximately 8 volumes of methyl chloride vapor per volume of catalyst space per minute, the temperature being maintained at 370° C. 47.5 per cent of the methyl chloride was decomposed. The product was analyzed as follows:

Product	Mols Carbon/100 mols CH_3Cl decomposed
CH_4	11.8
C_2H_4	4.0
C_3H_8	8.1
C_4H_{10} (Essentially iso)	22.9
C_2H_5Cl	2.3
C_5H_{12} (Essentially iso)	7.4
C_6H_{14} (Essentially iso)	4.1
C_7+	6.0
Carbon	33.4
	100.0

The C_4+ fraction was completely saturated which illustrates the effect of increasing the pressure on the degree of saturation of the product. The total yield of C_4+ product amounted to 40.4 per cent of the theoretical as compared with the yield of 28.8 per cent on a corresponding basis in Example 1 which was carried out at atmospheric pressure. Hydrocarbon product boiling above the C_4 fraction accounted for 17.5 mols of carbon per mol of 100 mols of methyl chloride decomposed. A greater proportion of the carbon of the methyl chloride feed appears in the C_4 fraction of the product than in Example 1 which C_4 fraction consists essentially of isobutane.

Example 3

A mixture containing 69 mol per cent of propane and 31 mol per cent of methyl chloride was passed over the above described alumina-silica gel actalyst at a space velocity of about 4.6 volumes of methyl chloride vapor plus propane per volume of catalyst space per minute and at a temperature of 425° C., atmospheric pressure being maintained in the reactor. 61.2 per cent of the methyl chloride was decomposed. The yields of products are given below:

Product	Mols Carbon/100 mols CH_3Cl decomposed
CH_4	7.6
C_2H_4	21.3
C_3H_6	20.9
C_4H_{10} (Essentially iso)	2.5
C_4H_8	4.6
C_5	7.0
C_6+	4.5
Carbon	31.4
	99.8

Comparing these results with the results obtained as described in Example 1 it is seen that considerably less methane and carbon is formed when propane diluent is used although a lower spaces velocity with respect to methyl chloride was used and the overall yield of hydrocarbons having more than one carbon atom is greatly increased by the presence of propane diluent. Particularly noteworthy is the relatively large amount of propylene appearing in the product. When this hydrocarbon is recycled large amounts of higher molecular weight normally liquid hydrocarbons are formed.

Example 4

A mixture of 51.1 mol per cent methyl chloride and 48.9 mol per cent of ethylene was passed over the alumina-silica gel catalyst at atmospheric pressure and 425° C. at a space velocity of 4.4 volumes of methyl chloride vapor plus ethylene per volume of catalyst space per minute. 44.4 per cent of the methyl chloride was decomposed to give the following yields:

Product	Mols Carbon/100 mols CH_3Cl decomposed
CH_4	6.8
C_2H_6	5.4
C_3H_6	40.1
C_2H_5Cl	2.6
C_4H_{10} (Essentially so)	8.9
C_4H_8	13.6
C_5	13.6
C_6	8.9
C_7+	7.2
Carbon	21.3
	128.4

Fourteen mols of ethylene for every hundred mols of methyl chloride decomposed entered the reaction. This effect is made evident by the total mols of carbon containing components in the product mixture. The product was highly unsaturated although the C_4+ fraction contained substantial proportions of isoparaffins. The product is similar to that obtained in Example 3 where propane was used as a diluent. The yield of C_5+ product is considerably higher while the free carbon is lower. Hence, it is advantageous to recycle ethylene, propylene, and propane as diluent.

Example 5

A mixture of 65.7 mol per cent of isobutane and 34.3 mol per cent of methyl chloride was passed over the above alumina-silica gel catalyst at 401° C., 300 pounds per square inch pressure and at a space velocity of 32.4 volumes of methyl chloride plus isobutane per volume of catalyst space per minute. 51.2 per cent of the methyl chloride was decomposed to yield the following products:

Product	Mols Carbon/100 mols CH_3Cl decomposed
CH_4	15.6
C_2H_4	4.1
C_3H_8	9.1
C_2H_5Cl	3.4
iC_5H_{12}	66.0
nC_5H_{12}	6.1
iC_6H_{14}	27.8
C_7+	7.0
Carbon	11.0
	150.3

Approximately 12.6 mols of isobutane were consumed per 100 mols of methyl chloride decomposed. In addition, a small fraction of the isobutane was isomerized to normal butane. The gasoline fraction was completely saturated and consisted primarily of a mixture of branched chain paraffins. However, the C_7+ fraction was rich in aromatics.

Comparing Examples 1 and 2 it is indicated that operation under pressure favors the production of paraffins rather than olefins. Thus, it can be seen that the recycle of ethylene, propane, and the C_4 fraction promotes the formation of normally liquid hydrocarbons and the

production of carbon is greatly decreased by the presence of such diluents.

This application is a continuation-in-part of our copending application entitled Catalytic conversion of normally gaseous hydrocarbons, Serial No. 556,746, filed October 2, 1944, now abandoned.

We claim:

1. The process for the conversion of methyl chloride to a mixture of normally liquid hydrocarbons which comprises the steps of (1) passing a feed stream consisting essentially of methyl chloride in contact with an alumina-silica catalyst in a reaction zone at a temperature within the range of from about 250° C. to about 500° C. to form a mixture comprising methane, normally gaseous paraffins higher than methane, normally gaseous olefins, unreacted methyl chloride, ethyl chloride and normally liquid hydrocarbons, (2) fractionating the product of step 1 to obtain a stream containing C_3 hydrocarbons, C_4 hydrocarbons, methyl chloride and ethyl chloride and a stream consisting essentially of normally liquid hydrocarbons, (3) fractionating the first mentioned stream of step (2) to separate therefrom propylene, ethyl chloride, and a methyl chloride-isobutane azeotrope, (4) recycling the propylene, ethyl chloride and methyl chloride-isobutane azeotrope from step 3 to step 1, and (5) recovering the normally liquid hydrocarbons from step 2.

2. The process for the conversion of an alkyl chloride feed stock consisting essentially of alkyl chlorides having less than four carbon atoms per molecule and consisting at least predominantly of methyl chloride which comprises the steps of (1) passing a feed stream consisting of said alkyl chloride feed stock through a reaction zone at a temperature within the range of from 250° C. to 500° C. in contact with a catalyst consisting of an association of silica with an oxide of a metal selected from the class consisting of aluminum, zinc, beryllium, gallium, magnesium, zirconium and thorium to form a product mixture comprising methane, normally gaseous normal paraffins, isobutane, normally gaseous olefins, unreacted alkyl chlorides, hydrogen chloride, and normally liquid hydrocarbons boiling in the gasoline range, (2) recycling at least a part of the olefins and the isobutane in the product effluent to the reaction zone, (3) recycling at least a part of the unreacted alkyl chlorides to the reaction zone, (4) recycling a sufficient part of the normally gaseous normal paraffins in the product effluent to maintain in the total feed to the reaction zone a mol ratio of hydrocarbons to total alkyl chlorides within the range of from about 0.5 to 1.0 to about 3.0 to 1.0 and (5) recovering the normally liquid hydrocarbons from the product effluent from step 1.

3. The process for the conversion of an alkyl chloride feed stock consisting essentially of alkyl chlorides having less than four carbon atoms per molecule and consisting at least predominantly of methyl chloride which comprises the steps of (1) passing a feed stream consisting of said alkyl chloride feed stock through a reaction zone at a pressure of from 15 to 40 atmospheres and at a temperature within the range of from 250° C. to 500° C. in contact with a catalyst consisting of an association of silica with an oxide of a metal selected from the class consisting of aluminum, zinc, beryllium, gallium, magnesium, zirconium and thorium to form a product mixture comprising methane, normally gaseous normal paraffins, isobutane, normally gaseous olefins, unreacted alkyl chlorides, hydrogen chloride, and normally liquid hydrocarbons boiling in the gasoline range, (2) recycling at least a part of the olefins and the isobutane in the product effluent to the reaction zone, (3) recycling at least a part of the unreacted alkyl chlorides to the reaction zone, (4) recycling a sufficient part of the normally gaseous normal paraffins in the product effluent to maintain in the total feed to the reaction zone a mol ratio of hydrocarbons to total alkyl chlorides within the range of from about 0.5 to 1.0 to about 3.0 to 1.0 and (5) recovering the normally liquid hydrocarbons from the product effluent from step 1.

4. The process for the conversion of methyl chloride to a mixture of normally liquid hydrocarbons which comprises the steps of (1) passing a feed stream consisting essentially of methyl chloride in contact with an alumina-silica catalyst in a reaction zone at a temperature within the range of from about 250° C. to about 500° C. and at a pressure of from about 15 to 40 atmospheres to form a mixture comprising methane, normally gaseous normal paraffins, isobutane, normally gaseous olefins, unreacted methyl chloride, ethyl chloride, and normally liquid hydrocarbons boiling in the gasoline range, (2) recycling at least a part of the olefins and the isobutane in the product effluent to the reaction zone, (3) recycling at least a part of the methyl chloride and ethyl chloride to the reaction zone, (4) recycling a sufficient part of the normally gaseous normal paraffins in the product effluent to maintain in the total feed to the reaction zone a mol of hydrocarbons to total alkyl chlorides within the range of from about 0.5 to 1.0 to about 3.0 to 1.0 and (5) recovering the normally liquid hydrocarbons from the product effluent of step 1.

5. The process of claim 2 in which the catalyst is alumina-silica.

6. The process of claim 3 in which the catalyst is alumina-silica.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,879,912	Schmidt et al.	Sept. 27, 1932
2,255,834	Carmody et al.	Sept. 16, 1941
2,364,762	Schmerling et al.	Dec. 12, 1944
2,417,119	Miller et al.	Mar. 11, 1947

OTHER REFERENCES

Lu et al., Ref. & Nat. Gas. Mfgr. 20, No. 9, pages 130–133.