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TREATMENT OF HYDROCARBON GASES

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This application is a continuation in part of my co-pending application Serial No. 677,081, filed June 22, 1933.

This invention refers more particularly to the treatment of hydrocarbon gases encountered in connection with the production and refining of petroleum including such gases as methane, ethane, propane, and the butanes which occur in natural gas, casinghead gases and refinery still gases and also olefinic gases produced as a result of cracking operations comprising such hydrocarbons as ethylene, propylene and the butylenes.

In a more specific aspect the invention is concerned with a particular process for pyrolyzing these normally gaseous hydrocarbons to form substantial yields of liquid hydrocarbons boiling within the range of gasoline in order to increase the percentage of gasoline recovered both from primary distilling and from cracking operations.

The light hydrocarbon gases referred to above occur in such large quantities that they are not readily consumed as fuel. The sale of propane and butane in cylinders for domestic and industrial purposes has provided a limited outlet for these gases and the corresponding olefins have been employed to a limited extent for the production of alcohols of an equal number of carbon atoms, these alcohols being of an iso or secondary character in the case of all hydrocarbons above ethylene. The market for these alcohols is somewhat limited as such and particularly because secondary alcohols are not as readily esterified as the normal alcohols and are, therefore, less readily utilizable in the manufacture of solvents and plasticizers for varnishes, automobile finishes, et cetera.

In one specific embodiment the present invention comprises the cracking at elevated temperatures and superatmospheric pressures of normally gaseous hydrocarbons to produce liquids of gasoline boiling range using as catalysts chlorine and certain chlorine compounds.

Among the compounds which may be employed alternatively with chlorine and among themselves (though not with exactly equivalent effects) to accelerate and modify the reactions of decomposition and polymerization occurring when hydrocarbon gases are subjected to elevated temperatures and pressures are hydrogen chloride, phosgene, carbon tetrachloride and various chlorinated hydrocarbons such as chloroform, monochlormethane, dichlormethane, dichlorethylene and chlorinated hydrocarbon mixtures obtained by reacting either chlorine or hydrochloric acid with low boiling hydrocarbons such as, for example, the olefins produced in cracking operations upon hydrocarbon gases or oils.

A noteworthy feature of the invention resides in the fact that the amounts of chlorine (either free or combined) which are necessary for promoting the reactions of decomposition and polymerization are relatively small, as will be specifically shown in a subsequent example. Thus, a positive advantage is obtainable in the direction of increased yield of gasoline boiling range liquids under a given set of conditions when amounts of chlorine, either as such or in combination, of the order of 0.1% are employed. While amounts as high as 1% of chlorine by weight may be employed, the optimum upper limit is usually below this point for several reasons, one being because the cost of chlorine becomes considerable, and another because too great an amount of chlorine fixation may occur so that chlorine compounds contaminate the desired liquid products. As a rule the efficiency of the process when adding chlorine increases up to a certain point and then diminishes so that the determination of the amount necessary for best results in the case of hydrocarbon gas mixtures of variable composition is in most cases a matter of trial. The exact function of chlorine and various chlorine compounds which may be employed alternatively is not entirely understood, though it is probable that the action is essentially catalytic and that the chlorine passes through a stage of intermediate compound formation, which intermediate compounds decompose to release chlorine or hydrogen chloride, or other chlorine compounds for further catalytic action while the liberated radicals are of increased energy content so that they combine to form the hydrocarbon polymers which are utilizable in motor fuel. In view of the lack of definite laws in the field of catalysis it is difficult to properly classify many reactions as to whether they are entirely catalytic or predominantly chemical, and no attempt in this direction will be made in the present instance.

Best results when utilizing chlorine and chlorine compounds to accelerate the decomposition and polymerization of hydrocarbons are commonly obtained within certain specific ranges of temperature and superatmospheric pressure, although the actual combination of temperature and pressure employed for a given hydrocarbon gas or mixture of hydrocarbon gases will need to be determined by trial after the selection of a chlorine compound for use as catalyst.

Temperature may be used within the range of about 900 to 1800° F. and higher if desired. The pressure factor is particularly important since, if too low pressures are used, there is a lessening of secondary polymerization reactions so that the ultimate yield of liquid products is below the maximum. In most cases a pressure somewhere between 400 and 1000 pounds per square inch is most suitable and good results have been obtained in the case of cracked hydrocarbon gas mixtures at pressure in the neighborhood of 750 pounds per square inch.

The chlorine or chlorine compounds of the general character already specified may be added to hydrocarbon gases undergoing cracking in any of the ordinary types of equipment, the introduction taking place either before the gases are heated, during their progress through tubular heating elements or, if necessary, in the reaction or soaking zones following the application of heat. Owing to the acceleration of the reactions the capacity of such equipment is noticeably increased and higher yields are made possible at moderate temperatures with a decreased formation of carbon and tarry deposits. The chlorine itself and gaseous chlorine compounds such as hydrogen chloride, phosgene, et cetera, may be released into the cracking zone from pressure containers while liquid compounds such as carbon tetrachloride and other chlorine-containing hydrocarbons may be brought up to the necessary pressure by small pumps.

An example of results obtainable by the use of the present process is given in the following data which shows increased yields of liquid products obtained when cracking propane at a temperature of approximately 1112° F., and a pressure of about 750 pounds to the square inch in a tubular heater:

Table I

	Pure propane	Propane+ 1% CCl_4	Propane+ 0.1% CCl_4
Liquid product			
Gal./1000 cubic ft. propane charged	0.82	2.0	1.7
Gal./1000 cubic ft. propane reacted	1.87	2.5	2.7
Blending octane number of product			118

Several points are worth noting in the tabulation. Primarily, of course, the increased yield of liquid product when using carbon tetrachloride mixed with propane is outstanding. Furthermore, it is to be observed that there is very little increased yield of liquid per 1000 cubic feet of propane charged when increasing the percentage of carbon tetrachloride from 0.1 to 1%. This increase from the standpoint of liquid produced per 1000 cubic feet of propane which actually underwent pyrolysis had a negative effect, since less liquid was produced with the higher percentage of catalyst. The blending octane number of the liquid is high, and this figure is merely given to show that the characteristics of the liquid produced using the carbon tetrachloride catalyst are essentially the same as those producible though at lower overall efficiency when operating without the present type of catalyst.

The particular nature of the invention is evident from the preceding specification and the example gives characteristic data in support of its value but neither is to be considered as imposing undue limitations on its generally broad scope.

I claim as my invention:

1. A process for producing liquid from normally gaseous paraffinic and olefinic hydrocarbons which comprises, subjecting the hydrocarbon gases to cracking temperature in the presence of a relatively small amount of chlorine not substantially in excess of 1% of the gas and under a pressure of from 400 to 1000 pounds per square inch.

2. A process for producing liquid from normally gaseous paraffinic and olefinic hydrocarbons which comprises, subjecting the hydrocarbon gases to cracking temperature in the presence of a relatively small amount of free chlorine not substantially in excess of 1% of the gas and under a pressure of from 400 to 1000 pounds per square inch.

3. A process for producing liquid from normally gaseous paraffinic and olefinic hydrocarbons which comprises, subjecting the hydrocarbon gases to cracking temperature in the presence of a relatively small amount of carbon tetrachloride not substantially in excess of 1% of the gas and under a pressure of from 400 to 1000 pounds per square inch.

4. A process for producing liquid from normally gaseous paraffinic and olefinic hydrocarbons which comprises, subjecting the hydrocarbon gases to cracking temperature in the presence of a relatively small amount of chlorine derivative of a hydrocarbon not substantially in excess of 1% of the gas and under a pressure of from 400 to 1000 pounds per square inch.

5. A process for producing liquid from normally gaseous paraffinic and olefinic hydrocarbons which comprises, subjecting the hydrocarbon gases to cracking temperature in the presence of a relatively small amount of chlorine not substantially in excess of 1% of the gas and under a pressure of approximately 750 pounds per square inch.

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