

March 6, 1956

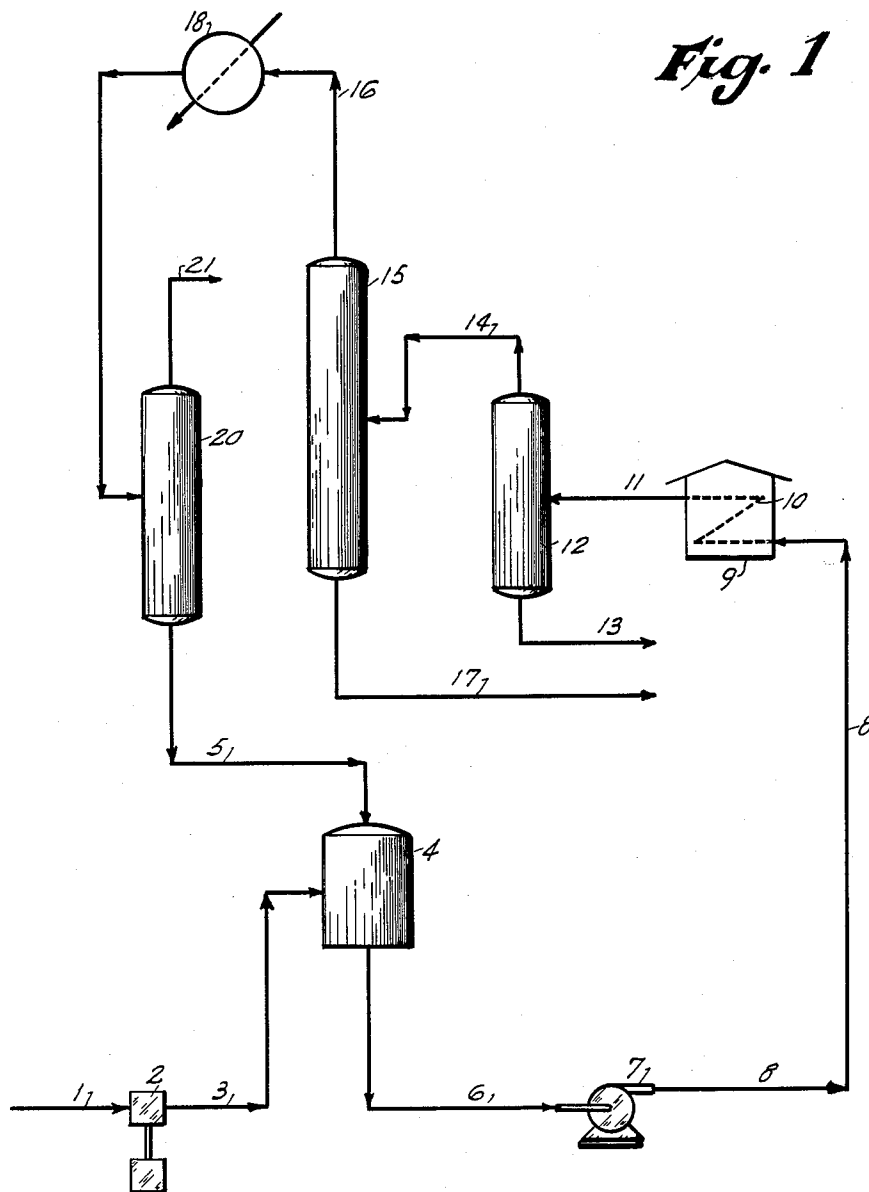
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CONTROL OF COKING IN THERMAL POLYMERIZATION

Filed Dec. 26, 1952

2 Sheets-Sheet 1



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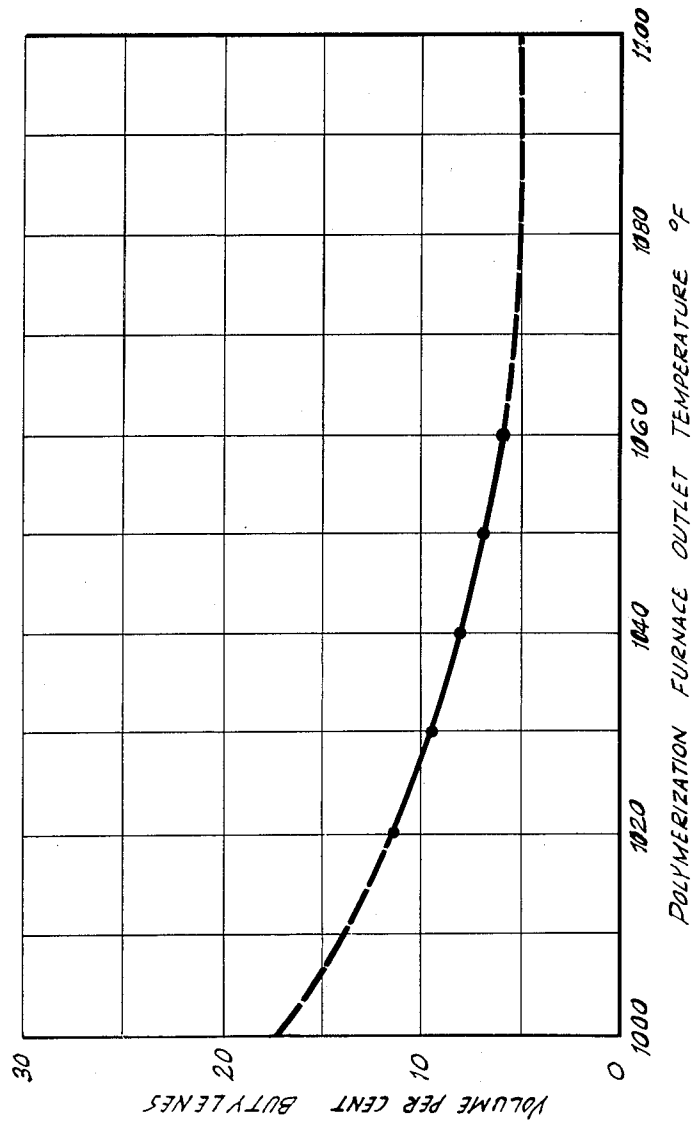
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2 Sheets-Sheet 2

Fig. 2



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CONTROL OF COKING IN THERMAL POLYMERIZATION

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Application December 26, 1952, Serial No. 327,983

1 Claim. (Cl. 260—683.1)

The present invention relates to the thermal polymerization of light hydrocarbons to form hydrocarbons boiling in the gasoline range and, more particularly, to a method of controlling the coke laydown in such a system of polymerization.

There are two general methods of thermally polymerizing light hydrocarbons to form hydrocarbons boiling in the gasoline range, (1) a method which light hydrocarbons, i. e., C₁ to C₄ hydrocarbons derived from the cracking of the feed stock or derived from an extraneous source are subject to thermal polymerizing conditions of temperature and pressure in the presence of naphtha or gas oil, and (2) a method in which light hydrocarbons, i. e., C₁ to C₄ hydrocarbons are subjected to thermal polymerizing conditions of temperature and pressure in the absence of any substantial amount of naphtha or gas oil. The light hydrocarbons can be obtained from any extraneous source such as a catalytic cracking operation.

In thermal polymerization of light hydrocarbons, coke is deposited in the tubes of the polymerization furnace to such an extent that the process must be interrupted at intervals to remove the coke deposited in the tubes of the polymerization furnace. As a consequence, one of the problems of thermal polymerization of light hydrocarbons to hydrocarbons boiling in the gasoline range is coke-free operation of the process for long periods of time. Heretofore it has been considered that the formation of coke in the thermal polymerization of light hydrocarbons to hydrocarbons boiling in the gasoline range is the result of the formation of tar and that the tolerable limit of tar production from a coking standpoint is about 1 to about 2 percent by weight of the furnace charge. In other words, approximately 2 per cent by weight of tar produced corresponds to incipient coke deposition. That is to say, when the tar produced represents about 2.5 weight per cent of the charge to the polymerization furnace, coke deposition proceeds rapidly. It follows that as long as tar production is held below about 2 per cent by weight of the furnace charge, little if any coke is produced over relatively long periods of time. However, when the tar produced amounts to about 2.5 weight per cent of the feed stock, the deposition of coke proceeds at such a rapid rate that the unit must be shut down to permit removal of the coke so deposited at such frequent intervals that the cost of operation becomes competitively excessive. Consequently, it has been the practice in the past to use the potential tar concentration in the feed stock as a means for controlling the production of coke in the polymerization furnace. That is to say, the severity of conditions in the polymerization furnace in the past has been controlled by determining how much tar will be produced from a given feed stock under standard conditions and then subjecting that feed stock to conditions of thermal polymerization, the severity of which was dependent upon the tar producing potential of the feed stock. However, this method of controlling the operation of a method for thermally polymerizing light hydrocarbons to hydrocarbons boiling in the gasoline range is not completely satisfactory. Use of the tar production value in

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controlling the thermal polymerization process for no-coke operation is unsatisfactory because, (1) the tar production value cannot be accurately measured due to gross inaccuracies involved in withdrawing a representative sample from the furnace effluent, and (2) coke laydown can proceed within the furnace due to excessive tar production without a significant increase in tar composition of the effluent; i. e., incremental production of tar can be converted to coke in the furnace tubes.

It has now been discovered that coke deposition can be correlated with the composition of the mixture of light hydrocarbons in the feed to the polymerization and particularly with the concentration of butylenes in the furnace charge. That is to say, the deposition of coke in the polymerization furnace can be controlled and held to a minimum by correlating the severity of the conditions of polymerization with concentration of butylenes in the charge to the polymerization furnace. Accordingly, it is an object of the present invention to subject light hydrocarbons, i. e., C₁ to C₄ hydrocarbons to conditions of thermal polymerization, i. e., temperature, pressure, and residence time, the severity of which is dependent upon the concentration of butylenes in the charge to the polymerization furnace. It is another object of the present invention to subject to polymerization conditions of maximum severity only those feeds to the polymerization furnace containing less than about 6 per cent by volume of butylenes. It is a further object of the present invention to subject feeds containing butylenes in amounts more than about 6 per cent by volume to reaction conditions of decreasing severity dependent upon the concentration of the butylenes in excess of about 6 volume per cent. It is also within the purview of the present invention to regulate the concentration of butylenes in the feed to a polymerization furnace to permit operation thereof under conditions of maximum severity to produce a maximum yield of hydrocarbons boiling within the gasoline range having the required octane rating.

For the purpose of illustrating the principles of the present invention, the thermal polymerization of light hydrocarbons, i. e., C₁ to C₄ hydrocarbons, in the absence of any substantial concentration of normally liquid hydrocarbons, to hydrocarbons boiling within the gasoline range has been selected. Accordingly, Figure 1 is a simplified schematic flow sheet of a thermal polymerization unit in which light hydrocarbons are thermally polymerized in the absence of any substantial concentration of normally liquid hydrocarbons; and Figure 2 is a graph showing the relation between the concentration of butylenes in the feed to the polymerization furnace and the maximum permissible severity of polymerization conditions therein for tolerable coke lay-down.

Referring first to Figure 2. The curve presented in Figure 2 exemplifies the relation between the concentration of butylenes in the charge to the polymerization furnace for conditions therein at which the coke lay-down can be tolerated for long time continuous operation. Tolerable coke lay-down is achieved when the feed contains not more than about 2.5, preferably 1.5 to about 2.0 weight per cent potential tar. Consequently, correlation of the concentration of butylenes in the charge to the furnace is correlated with furnace conditions of temperature, pressure and residence time which for that feed being charged will produce not more than the maximum tolerable coke lay-down during continuous operation for long periods of time while producing a gasoline having the required octane rating in maximum yield commensurate therewith. In other words, severity of conditions of polymerization being dependent upon temperature, pressure and residence time and since pressure and residence time in any particular unit are fixed within relatively narrow limits by design, the temperature is the one variable which can be changed over a relatively wide range. Accordingly, it follows that

the temperature employed for the polymerization is a measure of the severity of reaction conditions. In other words, as the reaction temperature is raised at a given reaction pressure and residence time, the severity of reaction conditions is increased. It follows that the graph presented in Figure 2 establishes that to maintain reaction conditions in the thermal polymerization of light hydrocarbons to hydrocarbons boiling in the gasoline range at maximum severity with tolerable production of coke, the severity, as measured by the outlet temperature of the effluent from the polymerization furnace, is increased as the concentrations of butylenes in the charge to the polymerization furnace decreases. Thus, at a reaction pressure of about 500 to about 3000 p. s. i., preferably about 1000 to about 2000 p. s. i., measured at the effluent outlet of the polymerization furnace, with a reaction temperature of about 900° to about 1150° F. and preferably of about 1020° to about 1080° F. as measured at the effluent outlet of the polymerization furnace and with a residence time at temperatures above 800° F. of about 10 to about 500, and preferably about 35 to about 175 seconds as measured by a cold oil velocity of about 3 to about 20, preferably about 5 to about 13, feet per second, a feed stock comprising light hydrocarbons containing about 11.5 volume per cent butylenes can be polymerized at a temperature of about 1020° F. without producing more than a tolerable amount of coke permitting continuous substantially coke-free operation of the polymerization furnace for long periods of time. On the other hand, under substantially the same reaction conditions of pressure and residence time, a feed stock comprising light hydrocarbons containing about 6 volume per cent butylenes can be thermally polymerized at a temperature of about 1060° F. without producing more than a tolerable amount of coke permitting continuous substantially coke-free operation of the unit for long periods of time. The shape of the curve presented in Figure 2 warrants the statement that a feed containing about 17 volume per cent butylenes requires a reaction temperature of about 1000° F. while at a concentration of butylenes of 6 volume per cent, or less, the reaction temperature can be raised to about 1100° F. Since with substantially constant reaction conditions in the polymerization furnace, the concentration of butylenes in the recycle remains substantially constant at any selected level of severity, the concentration of butylenes in the furnace charge can be regulated in accordance with the present invention by controlling the severity of reaction conditions of temperature, pressure and residence time in accordance with the concentration of butylenes in the light hydrocarbons admixed with the recycle to provide the feed to the polymerization furnace.

Of late years the demand for gasoline of higher octane rating has been increasing. This demand has lead to a more general use of the more severe reaction conditions. It is in this region of highest reaction severities that the greatest care must be exercised to correlate severity with the concentration of butylenes in the charge to the polymerization furnace. Thus, an increase of the concentration of butylenes in the fresh feed to the polymerization furnace from 5.75 volume per cent to 6.6 volume per cent requires lowering the severity of reaction conditions from that of 1060° F. to 1050° F. at substantially constant pressure and residence time.

Since the capacity of a polymerization furnace for a given residence time is fixed, the severity of reaction conditions can be correlated with the concentration of butylenes in the furnace charge most readily in one of two ways. That is to say, the octane rating of the gasoline to be produced being fixed and the concentration of butylenes in the charge being variable, maximum severity with tolerable coke lay-down can be obtained either by regulating the concentration of butylenes in the feed to a constant value dependent upon the furnace outlet temperature or more readily by regulating the furnace outlet temperature in correlation with the concentration of butyl-

enes in the furnace feed. However, when the required octane rating can only be achieved by operation at a severity above that at which tolerable coke lay-down for a feed containing the particular concentration of butylenes occurs, lowering of the concentration of butylenes as by the introduction of inert gases is a means of operating under the more severe furnace conditions without exceeding the tolerable coke lay-down.

Referring now to Figure 1 which is a simplified schematic flow sheet of a method of thermally polymerizing light hydrocarbons, C₁ to C₄ hydrocarbons, to hydrocarbons boiling in the gasoline range, light hydrocarbons from any suitable source such as a cracking reaction containing butylenes in a concentration dependent upon the severity of conditions of temperature, pressure and residence time existing in the polymerization furnace are drawn by pump 2 through line 1 and discharged at a reaction pressure of about 500 to about 3000 p. s. i. preferably about 1000 to about 2000 p. s. i. into line 3. The fresh feed under the aforesaid pressure enters accumulator 4 wherein it mixes with recycle introduced therein through line 5. The mixture of recycle and fresh feed in accumulator 4 is drawn through line 6 by pump 7 which discharges the mixture of recycle and fresh feed, i. e., furnace charge, into line 8. The furnace charge under the aforesaid pressure flows along line 8 to furnace 9 provided with coil or coils 10. While for simplicity only one furnace has been shown, it is common practice to pre-heat the furnace charge in one furnace and complete the heating of the furnace charge and at least a portion of the polymerization in a second furnace. The furnace charge after passing through the reaction zone, i. e., coils 10 of furnace 9 as illustrated, flows along line 11 to flash drum 12 wherein the tar drops out and is removed through outlet 13 while the lower boiling constituents of the effluent from the polymerization zone pass overhead through line 14 to depropanizer 15.

In depropanizer 15 a C₃-C₄ cut together with C₂ and lighter is taken overhead through line 16 while C₄ and heavier, i. e., gasoline are withdrawn through line 17 to after-treatment, storage, etc.

The C₃-C₄ cut taken overhead through line 16 flows to a condenser 18 wherein the C₂-C₄ are condensed. The condensed and uncondensed effluent from condenser 18 flows along line 19 to separator 20. In many commercial installations condenser 18 and separator 20 are combined in one unit.

In separator 20 the uncondensed gases C₂ and lighter together with any entrained C₃-C₄ separate from the condensate and are removed through line 21 to be further utilized while the condensate, i. e., C₃-C₄ recycle, is withdrawn through line 5 to pass to accumulator 4 to be mixed with fresh feed.

Accordingly, it is manifest that the description given hereinbefore is of a method of thermally polymerizing light hydrocarbons under thermal polymerizing conditions of temperature, pressure and residence time to produce a gasoline having a required octane rating and correlating the severity of said polymerizing conditions with the concentration of butylenes in the charge or feed to the polymerizing zone and that the concentration of butylenes in the feed to the polymerizing zone is correlated with the temperature thereof, so that for a charge to the polymerizing zone containing about 6 volume per cent or less butylenes, the outlet temperature of the polymerizing zone is at least about 1060° F. and for a charge to the polymerizing zone containing 10 volume per cent or more butylenes the outlet temperature of the polymerizing zone is less than 1030° F.

I claim:

A method of thermally polymerizing light hydrocarbons which comprises subjecting light hydrocarbons containing butylenes to conditions of thermal polymerization and regulating the temperature of polymerization for mixtures of light hydrocarbons containing not more than about 6 volume per cent butylenes to at least 1060° F. and for mix-

tures of light hydrocarbons containing more than about 6 volume per cent butylenes to temperatures less than 1060° F., said temperature decreasing from 1060° F. to 900° F. dependent upon increasing concentrations of butylenes in said light hydrocarbons.

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