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HYDROCARBON CONVERSION

Filed Nov. 30, 1959

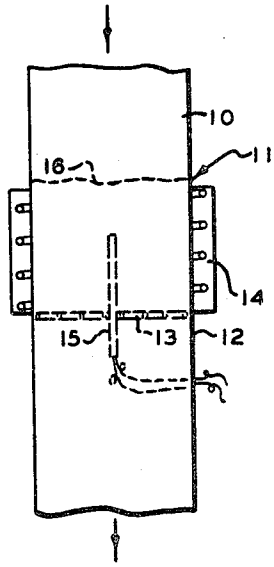



FIG. 1

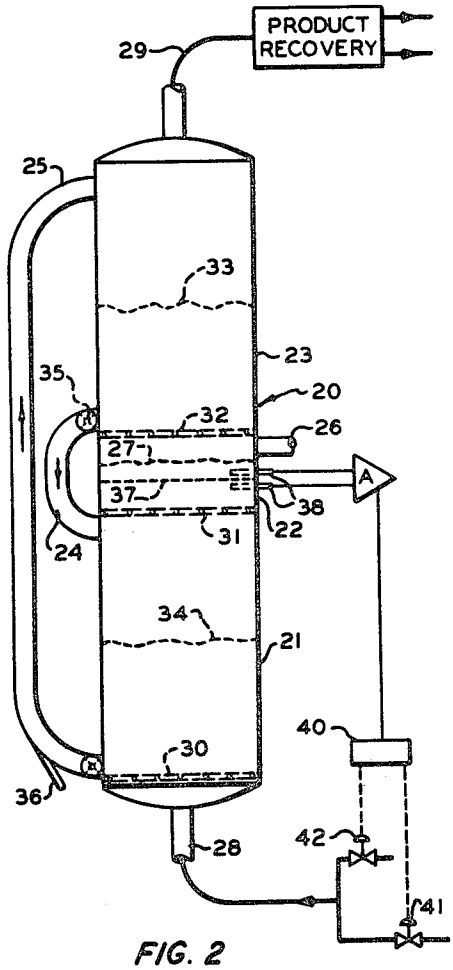



FIG. 2

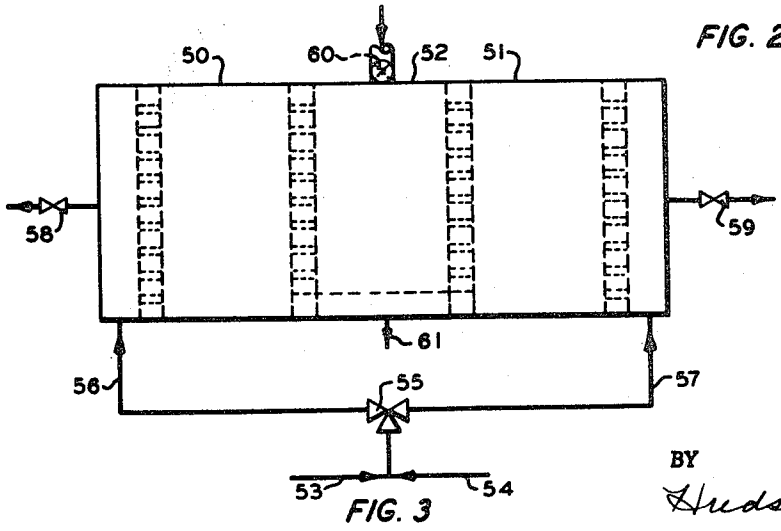



FIG. 3

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# HYDROCARBON CONVERSION

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2 Claims. (Cl. 260—683)

This invention relates to the pyrolysis of hydrocarbons and to the conversion of said hydrocarbons into hydrocarbons having a lower hydrogen content. In one aspect, this invention relates to a hydrocarbon converison process in which at least a portion of the heat required for the reaction is supplied by the oxidation of solid carbonaceous material in the presence of the hydrocarbon being converted. In another aspect, the invention relates to passing a mixture of a hydrocarbon and an oxygen-containing component through a bed of solid carbonaceous material under conditions such that oxidation of the carbonaceous material takes place, thereby supplying at least a portion of heat necessary for the conversion of hydrocarbon. In another aspect, the invention relates to a hydrocrabon conversion process in which at least a portion of the heat required for the process is supplied by oxidizing a solid carbonaceous material, said solid carbonaceous material being maintained in a fluidized bed in contact with said hydrocarbon. In another aspect, the invention relates to a hydrocarbon conversion process in which at least a portion of the heat required for the process is supplied by oxidizing a solid carbonaceous material in the presence of said hydrocarbon and transferring heat from a quench zone downstream of a reaction zone to a preheat zone upstream of said reaction zone. In another aspect, the invention relates to a hydrocarbon conversion process in which at least a portion of the heat of the reaction is supplied by oxidizing a solid carbonaceous material in the presence of the hydrocarbon in which the direction of flow through the reaction zone is reversed periodically to utilize heat extracted from the hydrocarbon leaving the reaction zone to pre-heat the hydrocarbon flowing to the reaction zone. In another aspect, the invention relates to reactor apparatus suited for use in endothermic reactions.

In the pyrolysis of hydrocarbons it is well known and has been customary to oxidize a portion of the feed stream while crackling the remainder. Thus, the oxidized portion of the feed supplies the heat of cracking necessary for converting the remainder of the feed. This process has been used for the conversion of paraffinic hydrocarbons to olefins. For example, such a process has been used for the preparation of ethylene from various gaseous feeds including methane, propane, ethane, and butane. In the prior art processes, oxygen, air or oxygen enriched air have been used as oxidants; co-current, counter-current, venturi and tangential mixing have been utilized to bring about the partial oxidation of the hydrocarbon feed; regenerative furnaces have been adapted to utilize the heat more efficiently in preheating the feed and quenching the reaction products. Such processes, however, have not been acceptable in certain areas where the feed material is in relatively short supply or must be imported. These processes have been disadvantageous both for economic reasons and by reason of government restrictions in some countries requiring a strict accounting of heat content of materials entering into a reaction process.

It is an object of the present invention to reduce the amount of hydrocarbon feed which must be oxidized to supply the heat for converting said hydrocarbon. Another object of this invention is to supply at least a portion of the heat necessary for hydrocarbon conversion process by oxidizing a solid carbonaceous material in the presence of the hydrocarbon feed converted. Another



object of this invention is to provide a hydrocarbon conversion process which results in the off-gas after separation of the product having a relatively high content of combustible material, thus making it suitable for use as a commercial heating gas. It is another object of this invention to provide a process in which an endothermic conversion is balanced by exothermic oxidation of a material other than the reactant. Another object is to provide improved apparatus suitable for use in endothermic processes.

Other aspects, objects, and the several advantages of the invention are apparent from a study of the disclosure, the drawing, and the appended claims.

Thus, my invention provides an improved process for the conversion of hydrocarbons in which heat is supplied to the process by oxidizing a solid carbonaceous material in the presence of the hydrocarbon being converted. This invention also provides a hydrocarbon conversion process comprising passing the hydrocarbon through a reaction zone containing solid carbonaceous material while simultaneously oxidizing the carbonaceous material. In one embodiment, the carbonaceous material is present in the form of a fluidized bed of solid particles.

My invention includes a hydrocarbon conversion process in which the hydrocarbon passes through adjacent preheat, reaction, and quench zones, and a portion of the heat supplied by oxidizing the solid carbonaceous material in the reaction is removed in the quench zone and transferred therefrom to the preheat zone. My invention further provides a hydrocarbon conversion process in which the hydrocarbon being converted passes through successive preheat, reaction, and quench zones, heat is supplied to the hydrocarbon in the reaction zone by the oxidation of solid carbonaceous material therein and heat is transferred from the quench zone to the preheat zone by cycling solid particles between the quench and preheat zones. My invention also provides a hydrocarbon converison process comprising periodically reversing the direction of flow of the hydrocarbon feed through a pair of regeneration zones, separated by a reaction zone in which heat is supplied to the hydrocarbon by oxidation of solid carbonaceous material.

My invention also provides apparatus suited for use in an endothermic process, the apparatus comprising a preheat chamber, a reaction chamber downstream of said preheat chamber, and a quench chamber downstream of said reaction chamber, a bed of solid carbonaceous material in said reaction chamber, and means to supply heat from asid quench chamber to said preheat chamber. In one embodiment, the means to supply heat comprises means to transfer solid particles cyclically between said quench and preheat chambers. My invention also provides apparatus comprising a pair of regeneration chambers separated by a reaction chamber, solid carbonaceous material in said reaction chamber, and means to oxidize said material and means to reverse the direction of flow of the hydrocarbon through said pair of regeneration chambers and said reaction chamber.

When the heat of an endotherermic hydrocarbon converison is supplied, according to my invention, by a carbon rich fuel such as coke, coal, charcoal, or other solid carbonaceous material, in a partial oxygenation reaction, the gaseous products contain relatively high proportions of hydrogen, carbon monoxide and methane, thus providing an off-gas, after separation of the conversion products, high in combustible material and being suitable for use as a commercial heating gas. For example, ethylene and propylene can consequently be maunfactured from propane in countries where the latter material must be imported, thus making it uneconomical to carry out the reaction by oxidizing a portion of the feed, and wherein government restrictions require an accounting

of heat content into a process and practically full conversion of the heat content to useful energy. Countries in which such restrictions are imposed and which also have adequate supplies of solid carbonaceous materials suitable for the practice of the invention include England, France, Germany, and Italy.

Hydrocarbons in general are adaptable for use as the feed in the practice of the present invention. However, although high aromatic feedstocks cannot be entirely omitted as possible feed constituents, hydrocarbon materials having predominantly paraffinic characteristics generally provide more desirable feedstocks. A further desirable characteristic is a relatively low viscosity. Thus, satisfactory feedstocks include normally gaseous hydrocarbons, naphthas boiling in the range of about 100° to 400° F., kerosenes boiling in the range of about 300° to 500° F., and light gas oils boiling in the range of 400° to 500° F. Such materials as diesel fuels and the various fuel oils can be used provided they have a viscosity and a boiling range suitable for the process.

It is well known that olefins can be prepared from the feedstocks outlined above by maintaining the temperature of the range of 1,250 to 1,700° F. I prefer to preheat the feed to the reaction zone to a temperature in the range of 500 to 1,000° F., and this can suitably be accomplished in most instances by arranging to transfer heat removed in a quench zone to the hydrocarbon feed.

In the practice of my invention there is developed within the solid carbonaceous material an incandescent zone. This zone can vary in various installations from 1 inch to 16 feet or more in height, the upper limit being determined by the weight of material which the burning zone will support. This limitation, of course, does not apply where the bed is fluidized.

The height of the incandescent zone can be controlled by varying the oxygen to hydrocarbon ratio and the rate of flow of the material through the bed. Suitable control means for the height of the incandescent zone are discussed below.

In the drawing, FIGURE 1 is a vertical cross section of a simplified apparatus suitable for practicing the process of my invention. FIGURE 2 is a vertical cross section of an apparatus suitable for use in a continuous process with continuous heat transfer from the quench zone to the inlet or preheat zone. FIGURE 3 is a vertical cross section of a reactor which permits utilizing heat removed in the quench zone by periodically reversing the direction of flow, thereby reversing the functions of the preheat and quench zones.

Referring now to FIGURE 1, this apparatus comprises inlet tube **10**, reaction chamber **11**, outlet tube **12**, perforated support **13**, heater **14**, and thermocouple **15**, and the perforated support **13** supports a bed **16** of solid carbonaceous material. In a specific embodiment used for experimental purposes, inlet tube **10**, reaction chamber **11**, and outlet tube **12** are all formed in a 17 mm. I.D. stainless steel tube.

In FIGURE 2 the reactor **20** comprises a preheat chamber **21**, a reaction chamber **22**, and a quench chamber **23**. Transfer tube **24** extends from the portion of chamber **23** adjacent chamber **22** to the portion of chamber **21** adjacent chamber **22**. Transfer tube **25** extends from the portion of chamber **21** removed from chamber **22** to the portion of chamber **23** removed from chamber **22**. An inlet **26** is provided for solid carbonaceous material which forms a bed **27** in chamber **22**. Reactant inlet **28** and product removal line **29** are provided as shown. A first perforated plate **30** is provided at the lower end of chamber **21**, a second perforated plate **31** divides chamber **21** from chamber **22**, and a third perforated plate **32** is provided at the lower end of chamber **23**. A bed **33** is maintained in chamber **23** of inert particles such as ceramic, metal or "Cermet." The latter denotes a group of materials made up of ceramic and metallic constituents, usually processed by powdered metallurgy techniques. They comprise, for example, borides of nickel, copper, barium, manganese and chromium; carbides of titanium, tantalum, columbium, molybdenum, vanadium, chromium, zirconium, and boron; the nitrides of silicon, titanium, zirconium, hafnium, vanadium, scandium, iobium, tantalum, tungsten, thorium, and uranium; and the silicides of calcium, manganese, iron, copper, boron, magnesium, vanadium, and titanium in combination with such ceramic-like materials as iron and aluminum oxide, titanium oxide, and the like.

Properties of these materials which may be used to an advantage, particularly when a fluidized operation is contemplated, are:

(1) Low attrition losses;

(2) High density and rapid heat transfer permitting high flow rates;

(3) High resistance to thermal shock; and

(4) A highly inert surface.

A similar bed **34** is maintained in chamber **21**. To transfer heat from chamber **23** to chamber **21**, inert particles are transferred continuously from chamber **23** to chamber **21** through transfer tube **24** and particles are transferred at the same rate from chamber **21** to chamber **23** through **25**. Flow through transfer tube **24** is by gravity, the rate being controlled by suitable means such as star valve **35**. The particles, of course, must be lifted through tube **25** and this can be done, for example, by using air lifting methods as by injecting air at **36**. Air or other oxygen-containing material may be introduced with a reactant through inlet **28** or may be passed directly into chamber **22** through suitable inlets not shown. An incandescent zone **37** is maintained within bed **27**. To control this zone, two light sensing elements such as phototubes **38** are positioned to see the area above and below the incandescent interface. When both the reactant and air are introduced through inlet **28**, a ratio controller **40** can be used to control the relative rates of flow of air through valve **41** and reactant through valve **42**. Phototubes **38** are connected to an amplifier which provides a signal to change the setpoint of ratio controller **40** to change the ratio of air to reactant and thus control the height of the incandescent zone. The phototube above the interface is normally inactive but if the interface rises to a point where this tube becomes illuminated, the ratio controller is activated to provide a richer mixture. The lower tube is positioned so that it normally sees the light. If the light intensity decreases below a predetermined value, the reduction of the amplifier response activates ratio controller **40** to provide a leaner mixture at inlet **28**. The construction and operation of the various components of the control system are well known and, therefore, need not be described in detail here.

An important variable in the conversion process of the present invention is the reaction time. For example, in the manufacture of olefins, reaction times in the range 0.001 to 2 seconds are utilized. When the height of the incandescent zone is established and the flow rate and feed to oxidant ratio are constant the reaction time remains constant. Reasonable variation in the reaction time is permissible within a desired range. However, in general, the reaction time should be established in the lower range when operating in the upper range of the temperature range and vice versa.

In FIGURE 3, chambers **50** and **51** are filled with refractory material and a bed of carbonaceous material is maintained in chamber **52**. Reactant and oxidant enter through lines **53** and **54**, respectively, and are directed by three-way valve **55** to inlet lines **56** and **57** alternately. When the flow is through line **56** the mixture enters chamber **50**, valve **58** being closed, and flows from there through reaction chamber **52** and through chamber **51** and out to product recovery through valve **59**. Suitable automatic temperature controllers, not shown, can be used if desired to operate valves **55**, **58**, and **59** and these

automatic controllers can in turn be actuated by the temperatures in chambers **50** and **51**. Periodically the direction of flow is reversed by reversing the position of three-way valve **55**, thus directing the flow through inlet **57** and removing the product through valve **58** to product recovery. It will be seen that this type of operation permits heat removal in either chamber **50** or **51** to be utilized to preheat the mixture when the flow is reversed. Suitable means for controlling the inlet of solid carbonaceous material to chamber **52** can be used such as star valve **60** and ashes can be removed through conduit **61** by suitable means, such as a conveyor, not shown.

In the operation of the present invention it has been found that the off-gas remaining after recovery of the olefins produced contains a relatively high concentration of hydrogen, carbon monoxide, and methane, thus making it suitable for use as a commercial heating gas. Ethylene and propylene can, therefore, be manufactured from propane, for example, in countries where the latter material must be imported and government restrictions require an account of heat content of materials entering into a process and practically full conversion of this heat content to energy.

A hypersorption recovery system can be advantageously employed in the separation of the olefin product from the off-gas. However, it is also possible to use more conventional fractionation systems if desired.

In one example of the invention, a 40 millimeter vertical Vycor tube 20 inches long was packed with 5 inches of inert (non-catalytic) ceramic spheres. On this inert support was placed a bed of wood charcoal 8 inches deep. The charcoal was broken, classified, and only those pieces falling in the particle size range of ⅛ inch to ¼ inch were utilized. Propane and air mixture flowing at the rate of 0.834 standard cubic feet per hour propane and 10.25 standard cubic feet per hour of air were admitted to the bottom of the packed section and ignited. Under these conditions, the bottom of the charcoal layer became red hot for a height of one inch and stabilized. Samples of off-gas were collected representing the stabilized reaction products. Table I gives the analysis of the composite sample collected.

*Table I*

| Constituent | Mol percent | Constituent | Mol percent |
|---|---|---|---|
| $H_2$ | 11.1 | $CH_4$ | 2.3 |
| $N_2$ | 57.5 | Ethylene | 1.2 |
| CO | 16.5 | Propylene | 0.4 |
| A | 0.8 | Ethane | 0.2 |
| $CO_2$ | 8.9 | Propane | 0.9 |

This analysis indicates that 28 percent of the propane was being converted to olefins (ethylene+propylene) and that 68 percent of the CO and $CO_2$ originated from the charcoal.

In a second run, the same tube was utilized as in the first run. The charcoal bed had been reduced in height to 6.5 inches. Propane at the rate of 2.64 standard cubic feet per hour and air at the rate of 30.2 standard cubic feet per hour were charged to the bottom of the packed section. The red hot zone in the charcoal bed stabilized at a height of approximately 3 inches. Analysis of the off-gas collected as a composite sample is given in Table II.

*Table II*

| Constituent | Mol percent | Constituent | Mol percent |
|---|---|---|---|
| $H_2$ | 12.8 | $CH_4$ | 2.9 |
| $N_2$ | 56.8 | Ethylene | 1.7 |
| CO | 17.9 | Propylene | 0.1 |
| A | 0.7 | Ethane | 0.1 |
| $CO_2$ | 6.8 | Propane | 0.1 |



This analysis indicates that 29 percent of the propane was converted to olefins and that 52 percent of the CO and $CO_2$ came from the combustion of charcoal.

These results were especially promising because no attempt had been made to compensate for the gross heat losses from the reaction zone, a somewhat different arrangement of apparatus was utilized. FIGURE 1 shows the details of the apparatus. A 17 millimeter I.D. stainless steel tube was utilized for this run. A water saturated mixture of 70.8 percent propane and 29.2 percent air at a rate of 206 standard cubic feet per hour per square foot was charged to the top of the tube. Near the center of the tube, a stainless steel fritted disk approximately ⅛ inch thick supported a bed of crushed wood charcoal having a particle size in the range through a ⅛ inch mesh and retained on a 32-mesh screen. Below the fritted disk a thin-walled stainless tubing containing thermocouple leads traversed the lower, unpacked, reactor tube, pierced the fritted disk and terminated within the charcoal bed approximately ¾ inch above the top of the fritted disk. The thermocouple junction was welded to the closed end of the stainless tubing and was packed with swaged magnesia. A resistance heater was placed around the section containing the charcoal for a distance of one and one-fourth inches above the upper surface of the fritted disk. The reaction zone was preheated to a temperature of approximately 1,400° F. as measured by the thermocouple. The gas was ignited and after a brief period of fluctuation the temperature, as measured by the thermocouple, lined out at 1,385±5° F. which was probably within the limit of accuracy in measuring the temperature. A sample taken after conditions had stabilized indicated the following off-gas composition.

*Table III*

| Constituent | Mol percent | Constituent | Mol percent |
|---|---|---|---|
| $H_2$ | 15.1 | $CH_4$ | 12.1 |
| $N_2$ | 19.7 | Ethylene | 10.5 |
| CO | 3.6 | Ethane | 0.9 |
| A | 0.3 | Propylene | 7.3 |
| $CO_2$ | 1.7 | Propane | 26.8 |
| $O_2$ | 1.5 | Butylenes | 0.3 |

These data indicate that approximately 28 percent of the propane charged is converted to olefins, but more than ¼ of the propane will be available for recycle after recovery of the olefins which indicates that greater ultimate yields will be experienced. The analysis indicates that the off-gas would have an available heat content of approximately 376 Btu. per cubic foot. However, if oxygen was substituted for air a value approaching 837 Btu. per cubic foot could be attained. Values between these extremes could be attained by operating with oxygen-enriched air.

When it is desired to use a fluidized bed of solid carbonaceous material for the practice of this invention, control of the reaction time is accomplished through control of the depth of the fluidized bed since, through the fluidizing action, the bed may be incandescent throughout its depth. Control of the fluidized bed is accomplished by controlling one or more of (1) the amount of solid carbonaceous material present in the bed at a given time and (2) the amount and rate of flow of fluidizing gas in the bed. The amount of material in the bed is, of course, controlled by regulating the flow of solid carbonaceous material into and out of the reaction zone. The fluidizing action within the zone is controlled by regulating the flow of reactant and/or oxidizing gas, either of which may be controlled in conjunction with or independent of the other. Thus, use of a fluidized bed permits a very flexible operation in that control of the reaction time can be obtained with some degree of independence of the other reaction vairables. It will be recognized that those

skilled in the art of fluidized bed reactions can effect such controls given the teaching of the present disclosure.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, the drawing, and the appended claims to the invention, the essence of which is a hydrocarbon conversion process in which at least a portion of the endothermic heat of the reaction is supplied by oxidizing a solid carbonaceous material in the presence of the hydrocarbon being converted; the control of the reaction time is obtained by controlling the height of an incandescent zone of the solid carbonaceous material and the rate of flow of hydrocarbon through the reaction zone, a fluidized bed is provided in which the height of the incandescent zone is controlled by controlling the depth of the bed; and apparatus for performing endothermic reactions.

I claim:

1. A hydrocarbon conversion process, comprising the steps of:

passing a hydrocarbon through a reaction zone in contact with a bed of solid carbonaceous material contained therein, under conditions to effect an endothermic conversion of said hydrocarbon;

igniting said bed;

simultaneously passing a sufficient amount of an oxidizing agent with said hydrocarbon through said bed to oxidize exothermically a sufficient quantity of said solid carbonaceous material to provide and maintain an incandescent zone within said bed, to maintain desired operating temperature continuously, and to supply a major portion of the heat required for the endothermic conversion of said hydrocarbon; and

controlling the reaction by controlling the height of said incandescent zone and the rate of flow of said hydrocarbon through said zone.

2. A hydrocarbon conversion process, comprising the steps of:

passing a hydrocarbon through a reaction zone in contact with a bed of solid carbonaceous material contained therein, under conditions to effect an endothermic conversion of said hydrocarbon;

igniting said bed;

simultaneously passing a sufficient amount of an oxidizing agent with said hydrocarbon through said bed to oxidize exothermically a sufficient quantity of said solid carbonaceous material to provide and maintain an incandescent zone within said bed, to maintain desired operating temperature continuously, and to supply a major portion of the heat required for the endothermic conversion of said hydrocarbon; and

controlling the reaction by controlling the height of said incandescent zone by sensing the height from the upper level of said incandescent zone and reducing the ratio of oxidizing agent to hydrocarbon when the height exceeds the desired height, and increasing the ratio of oxidant to hydrocarbon when the height falls below the desired height, while maintaining the rate of flow of said hydrocarbon through said zone at a predetermined value.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 1,972,898 | Odell | Sept. 11, 1934 |
| 2,684,390 | Bills | July 30, 1954 |
| 2,752,407 | Cahn | June 26, 1956 |
| 2,767,233 | Mullen et al. | Oct. 16, 1956 |
| 2,790,838 | Schrader | Apr. 30, 1957 |
| 2,824,148 | Keulemans et al. | Feb. 18, 1958 |
| 2,870,087 | Gilmore | Jan. 20, 1959 |