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HYDROCARBON CONVERSION

Milton M. Marisic, Elgin, and Harvey Hennig, Cary, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

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This invention relates to the thermal conversion of normally gaseous hydrocarbons. A more particular aspect of this invention relates to improved thermal conversion processes whereby C_2 to C_5 hydrocarbons are converted to valuable gaseous and liquid hydrocarbon products.

In the refining of petroleum and the production of petroleum products from oil wells, a large amount of normally gaseous hydrocarbon by-products are produced. These gases result from many hydrocarbon conversion processes, such as cracking, reforming, and other liquid hydrocarbon treating processes. In addition to refinery gases, a large volume of normally gaseous hydrocarbons also results from processes for the recovery of natural gasoline from the products of condensate wells. Normally gaseous hydrocarbons recovered from these various sources are ordinarily composed of a major proportion of methane and ethane and lesser proportions of propane, propylene, n-butane, i-butane, butenes, and other gases containing 2 to 5 carbon atoms. In order to make the over-all refinery procedure economically sound, these waste gases and other normally gaseous products must be utilized or converted to more valuable products. A limited amount of normally gaseous hydrocarbons can be liquefied and employed as a fuel for household purposes and in certain types of vehicles. However, the market for liquefied hydrocarbon gases is not sufficient to utilize all gases produced by the petroleum industry and, in addition, some form of preliminary purification must be practiced in order to recover a suitable liquefiable gas. In addition to the liquefaction of hydrocarbon gases, valuable petrochemicals and petrochemical intermediates can also be produced from pure and mixed hydrocarbon gases. Chief among the hydrocarbon products which can be produced for the petrochemical industry are ethylene and acetylene. In order to obtain these olefinic hydrocarbons from gaseous mixtures, it has been the practice in the petroleum art to subject the gaseous mixture to pyrolysis with or without catalysts to convert higher olefins to olefins having fewer carbon atoms and to convert the paraffin content of the gaseous mixture to olefins. During the course of a process for the conversion of gaseous hydrocarbons by pyrolysis, both cracking and dehydrogenation take place. Thus, higher paraffins and olefins, such as propane and propylene, may be cracked to produce ethylene, and paraffins, such as ethane, may be simultaneously dehydrogenated to produce ethylene. A second type of process which has been used in the conversion of gaseous hydrocarbons to valuable hydrocarbon products is the conversion of such gaseous mixtures to gasoline by thermal or catalytic polymerization processes. In this type of conversion, cracking and dehydrogenation of hydrocarbon gases also take place, and the olefins resulting from this cracking and dehydrogenation are then polymerized to produce hydrocarbons boiling in the gasoline range. The present invention is directed primarily to thermal conversion

processes of the type mentioned above and to methods of improving these processes.

In conducting a process for the thermal conversion of pure gaseous hydrocarbons or hydrocarbon gas mixtures to produce olefins, such as ethylene, extremely high temperatures in the range of about 1400° to 1500° F. are generally employed. The hydrocarbon gases to be converted are subjected to this temperature for a period of approximately 0.7 to 1.3 seconds at a pressure of about 10 to 30 pounds per square inch gauge. Under these conditions, the primary products of the reaction will be an olefinic gas having a high ethylene content. By permitting gaseous hydrocarbons to be exposed to slightly lower temperatures for longer periods of time and under much higher pressures, the olefins formed during the primary reaction, illustrated by the conversion of gaseous hydrocarbons to ethylene, can be converted to products having a substantial content of high quality gasoline components. This latter process is termed thermal polymerization and is ordinarily carried out at pressures of approximately 60 to 3000 pounds per square inch guage and a temperature of about 900° F. to 1150° F. for a period of one minute or more. Thus, it may be seen that the conditions required for the conversion of normally gaseous hydrocarbons to valuable gaseous and liquid products are extremely severe and require the use of relatively expensive conversion equipment manufactured from materials capable of withstanding extreme reaction conditions. In addition, the yields of gaseous olefins and gasoline per pass obtained by such processes are relatively low. For example, ethylene yields in the range of substantially less than 25 per cent by weight of the total feed gas are not uncommon in the conversion of a mixture of C_2 to C_5 hydrocarbons.

It is, therefore, an object of this invention to provide an improved process for the thermal conversion of normally gaseous hydrocarbons.

Another object of this invention is to provide an improved process for the thermal conversion of C_2 to C_5 hydrocarbons to valuable gaseous and liquid hydrocarbon products.

It is another and further object of this invention to provide an improved process for the thermal conversion of C_2 to C_5 hydrocarbons whereby increased product yields are obtained.

Still another object of this invention is to provide a process for the thermal conversion of C_2 to C_5 hydrocarbons which may be carried out at temperatures substantially below those conventionally employed without reducing product yields.

Another and further object of this invention is to provide a process for the thermal conversion of C_2 to C_5 hydrocarbons wherein shorter reaction times may be employed without reducing product yields.

A further object of this invention is to provide a process for the thermal conversion of C_2 to C_5 hydrocarbons wherein reaction temperatures may be reduced and shorter reaction times may be employed without reducing product yields.

Another object of this invention is to provide a process for the thermal conversion of C_2 to C_5 hydrocarbons wherein the effective life of reaction equipment may be extended.

Still another object of this invention is to provide a process for the thermal conversion of C_2 to C_5 hydrocarbons wherein relatively inexpensive reaction equipment may be employed.

Other and further objects of this invention will be apparent from the following description of our invention.

It has been found in accordance with the present invention that increased product yields or, in the alternative,

reduced requirements of temperature and contact times may be attained in a process for the thermal conversion of C_2 to C_5 hydrocarbons by carrying out the conversion in the presence of a small amount of a normally non-gaseous hydrocarbon which will crack more readily than the gaseous hydrocarbon feed stocks. In accordance with a more specific aspect of the present invention, it has been found that, by adding a small amount of a predominantly paraffinic hydrocarbon having at least 7 carbon atoms per molecule to C_2 to C_5 hydrocarbon gases undergoing thermal conversion, substantial increases in the product yields may be obtained.

Although it is not desired to limit the scope of the present invention by any theoretical explanation of the reasons for the improved results obtained by practicing this invention, it is believed that the advantages attained by following the teachings of the present invention may be explained by a brief discussion of the free radical theory of hydrocarbon conversion. This theory of hydrocarbon conversion was proposed by F. O. Rice and is explained in the Journal of the American Chemical Society, volume 53, pages 1959–1972, 1931; volume 55, pages 3035–3040, 1933; and volume 65, pages 590–595, 1943. In accordance with the free radical theory of the thermal decomposition of hydrocarbons, the decomposition of butane to a product containing ethylene is thought to proceed in accordance with the following four steps:

1. Rupture of a bond in a molecule to produce two free radicals:

$$CH_3-CH_2-CH_2-CH_3 \longrightarrow CH_3-CH_2\cdot + CH_3-CH_2\cdot$$
$$\searrow\ CH_3-CH_2-CH_2\cdot + CH_3\cdot$$

2. Reaction between free radicals and molecules:

$$CH_3-CH_2-CH_2-CH_3 + CH_3-CH_2\cdot \rightarrow CH_3-CH_2-CH\cdot-CH_3 + CH_3-CH_3$$
$$\searrow\ CH_3-CH_2-CH_2-CH_2\cdot + CH_3-CH_3$$

3. Decomposition of large free radicals:

$$CH_3-CH_2-CH\cdot-CH_3 \longrightarrow CH_3\cdot + CH_2=CH-CH_3$$
$$CH_3-CH_2-CH_2-CH_2\cdot \longrightarrow CH_3-CH_2\cdot + CH_2=CH_2$$
$$CH_3-CH\cdot-CH_3 \longrightarrow H\cdot + CH_3-CH=CH_2$$

4. End of chain, reaction of two radicals by combinations or disproportionation:

$$CH_3\cdot + H\cdot \longrightarrow CH_4$$
$$CH_3\cdot + CH_3\cdot \longrightarrow CH_3-CH_3$$
$$CH_3\cdot + CH_3-CH_2-CH_2\cdot \longrightarrow CH_2=CH_2 + CH_3-CH_3$$

Also, in accordance with this theory, steps 2 and 3 can be repeated any number of times, each time regenerating a free radical to permit repetition of the cycle. Thus, it may be seen that the amount of conversion depends to a certain extent upon the number of cycles which take place in accordance with steps 2 and 3 before step 4 ends the process. Thus, it is believed that in the thermal conversion of normally gaseous hydrocarbons the addition of a small amount of a hydrocarbon material which is more easily cracked than the hydrocarbon feed gases results in the production of a large number of free radicals in the conversion zone, thus increasing the number of free radicals which react with the normally gaseous hydrocarbons as represented by steps 2 and 3 and concomitantly increasing the yield of desirable products during a given time interval.

In order to illustrate the advantages of the present invention, a number of examples will be given illustrating the magnitude of the increase in yields of ethylene which are obtained in the conversion of various hydrocarbon gases when such processes are carried out in the presence of small amounts of a normally non-gaseous hydrocarbon sensitizer. The non-gaseous hydrocarbon sensitizer, as contemplated by the present invention, is a predominantly paraffinic hydrocarbon material or mixture of hydrocarbons having more than 7 carbon atoms per molecule and characterized by being more readily cracked than the gaseous hydrocarbons which are to be converted. Still more specifically, it is preferred that the hydrocarbon sensitizer have a UOP characterization factor higher than 12 and an aniline point greater than 150° F. A hydrocarbon sensitizer which has been found eminently suitable for use in accordance with the present invention is a soft wax obtained as a by-product in the manufacture of paraffin and microcrystalline waxes from petroleum. Other predominantly paraffinc petroleum products, such as crystalline wax, petrolatum, etc., may also be employed. These materials are preferably employed in amounts of from one to ten per cent by weight based on the amount of gaseous hydrocarbon feed.

For example, in the cracking of propane at 1300° F., wherein an equivalent contact time of one second is employed and the pressure maintained at approximately atmospheric pressure, a conversion of 22.9 per cent per pass of the propane feed is obtained. By employing a mixture of 1.22 mol per cent or 3.1 per cent by weight of normal octane and 98.78 mol per cent or 96.9 per cent by weight of propane in the cracking unit, a conversion of approximately 23.5 per cent per pass of total feed is obtained. Thus, by carrying out the conversion in the presence of a non-gaseous hydrocarbon sensitizer of the present invention, an increase in ethylene production of about 2.6 per cent is obtained.

Since higher molecular weight paraffinic hydrocarbons yield free radicals more readily than those of lesser molecular weight, the use of higher molecular weight paraffins as sensitizers increases the conversion of the C_2 to C_5 gaseous feed even more. This is illustrated by the following example where propane is cracked in the presence of 3.1 weight per cent soft wax instead of 3.1 weight per cent normal octane. Cracking of propane in the presence of 0.5 mol per cent or 3.1 per cent by weight of soft wax under the same conditions as those employed above results in an increase of about 12.3 per cent in the yield of ethylene in comparison to the yield obtained by cracking under the same conditions in the absence of a sensitizer.

The superiority of employing a sensitizer such as soft wax is shown more clearly when data of the first two examples are applied to a commercial size plant. A plant charging propane as fresh feed is so operated that with a fresh feed of 4,580 lb./hr. propane, and a total feed of 20,000 lb./hr., including recycle, the ethylene production amounts to 1,910 lb./hr. When operating this same plant at the same conditions of temperature, pressure, and total furnace charge by weight, but employing 3.1 per cent by weight of soft wax, based on total furnace charge, as sensitizer, the fresh feed now is 5,176 lb./hr., including the soft wax feed amounting to 620 lb./hr., and the ethylene yield amounts to 2,148 lb./hr. Thus, by employing the sensitizer it is possible to increase conversion of the feed so that under similar operating conditions a greater amount of fresh feed can be charged and a greater amount of ethylene can be produced without enlarging the pyrolysis coil. For this plant the increase in production would amount to over one million pounds per year.

In a third example, the effect of employing a small amount of a sensitizer in the dehydrogenation of ethane to produce ethylene is illustrated. Dehydrogenation of pure ethane at 1420° F., under a pressure of about 30 pounds per square inch gauge and for an equivalent contact time of one second, gives an ethylene yield of approximately 31.3 per cent by weight of the total feed gas. By carrying out the reaction under the same conditions and adding 2 per cent by weight of soft wax as the sensitizer, an ethylene yield of 34.1 per cent by weight of the total feed gas is obtained. Thus, an over-all increase of 8.9 per cent by weight of ethylene is obtained when the sensitizer of the present invention is employed.

From the examples set forth above, it may be seen

that substantial increases in the yield of ethylene are obtained in the cracking or dehydrogenation of normally gaseous hydrocarbons by employing a small amount of the sensitizer of the present invention. These increases in yield are also obtained in other processes for the thermal conversion of normally gaseous hydrocarbons, such as the thermal polymerization of C_2 to C_5 hydrocarbons. By adding a small amount of soft wax or other suitable sensitizer to the normally gaseous hydrocarbon feed to a thermal polymerization zone, increased yields of high quality gasoline may be obtained. The reaction mechanism responsible for the advantages attained by employing the sensitizer of this invention in a polymerization reaction is believed to be similar to that propounded for the thermal decomposition of butane and can be illustrated by the following steps:

1. Rupture of a bond in a molecule to produce two free radicals:

$$CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_3\cdot + \cdot CH_2{-}CH{=}CH_2$$

2. Combination of a free radical and an olefin molecule to form a larger free radical:

$$\cdot CH_2{-}CH{=}CH_2 + CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_3{-}CH_2{-}\underset{\displaystyle CH_2\cdot}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH_2$$

3. Reaction between larger free radicals and an olefin:

$$CH_3{-}CH_2{-}\underset{\displaystyle CH_2\cdot}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH_2 + CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH_2 + CH_3{-}\dot{C}H{-}CH{=}CH_2$$

4. End of chain, reaction of two free radicals:

$$CH_3{-}\dot{C}H{-}CH{=}CH_2 + CH_3\cdot \longrightarrow CH_3{-}CH(CH_3)CH{=}CH_2$$

As in the thermal decomposition reaction, steps 2 and 3 can be repeated a number of times, each time converting a molecule and at the end of step 3 regenerating a free radical which can again react according to steps 2 and 3. Thus, by the addition of a sensitizer in accordance with this invention, the number of free radicals which react with the normally gaseous hydrocarbons, as represented by steps 2 and 3, is increased and the yield of polymer gasoline is increased.

In order to illustrate the advantages of carrying out a thermal polymerization reaction in the presence of the sensitizer of this invention, the results of a series of parallel polymerization reactions are given below. In this series of runs, a feed gas of the following composition is employed:

Constituent:	Weight percent
CH_4	1.8
C_2H_4	6.4
C_2H_6	3.4
C_3H_6	19.2
C_3H_8	30.2
C_4H_8	19.2
C_4H_{10}	19.8
	100.0

under the following conditions:

Run	A	B	C
Sensitizer	None	n-octane	soft wax
Molecular weight		114.2	280
Amount, wt. percent of total fresh charge		2.37	2.37
Amount, mol percent of total fresh charge		1.0	0.41
Average reactor temperature, °F	1,055	1,055	1,055
Average reactor pressure, p. s. i.	1,000	1,000	1,000
Approximate time of contact, seconds	80	80	80
Feed, lb./hr.:			
Fresh C_2–C_5 hydrocarbons	4,380	4,471	4,969
Sensitizer		109	121
Total fresh feed	4,380	4,580	5,090
Recycle	32,620	32,420	31,910
Total feed	37,000	37,000	37,000

and the following results are obtained:

Run	A	B	C
Products:			
Fuel gas, lb./hr.	680	714	833
C_5–400° F. polymer, barrels/day	324	338	366
Tar (400° F.+), barrels/day	20	21	29
Based on run A:			
Increase in C_5–400° F. polymer—			
vol. percent		4.4	12.8
bbl./day		14	42
Increase in fresh C_2–C_5 hydrocarbon charge—			
lb./hr.		91	589
wt. percent		2.1	13.4
Increase in total fresh feed—			
lb./hr.		200	710
wt. percent		4.6	16.2

From the data appearing above, it is evident that the use of a sensitizer in accordance with the present invention results in an increase in the reaction rate and the yield of polymer gasoline.

It will be obvious to one skilled in the art that following the teachings of the present invention will result in outstanding advantages other than an increase in the yield of the desired product. For example, greater through-put of feed gases may be practiced under prior art conditions of temperature and pressure without detrimentally affecting the yield of the desired products. Likewise, the temperatures employed in a conversion process may be reduced while maintaining conventional pressures and contact times. It may also be seen that by carrying out the thermal conversion process at reduced temperatures great economical advantages result from lengthened reaction equipment life or the use of equipment constructed to withstand less demanding reaction conditions.

As has been pointed out above, the severity of the conditions heretofore employed in the thermal conversion of gaseous hydrocarbons may be substantially reduced by carrying out the reaction in the presence of a small amount of a sensitizer in accordance with the present invention. However, when it appears more advantageous to direct the process toward the attainment of maximum product yields from a given quantity of hydrocarbon gases, the reaction conditions employed in the prior art may be employed. For example, in the thermal conversion of a mixture of C_2 to C_5 hydrocarbons, wherein the desired product is a gaseous olefin, such as ethylene, it is preferred to employ a temperature of about 1480° F., an average pressure of about 14 pounds per square inch gauge and a reaction time of approximately one second. On the other hand, where the desired product of the thermal conversion is liquid hydrocarbons boiling in the gasoline range, preferred conditions include: a temperature of 1050° to 1100° F., a pressure of about 1200 pounds per square inch gauge, and a reaction time of one minute or more.

Introduction of the sensitizer into the reaction zone may also be varied to meet individual requirements or preferences. For example, in the cracking of C_2 to C_5 hydrocarbons to produce olefins, the sensitizer may be injected into the pyrolysis coil at the beginning of the radiant section or at a plurality of points in the coil more or less evenly distributed throughout the radiant section of the pyrolysis coil. When operating in the latter manner, it is also possible to employ more than one sensitizer. That is, a sensitizer which is readily cracked, such as soft wax, is injected into the pyrolysis coil at the beginning of the radiant section and a more stable sensitizer, such as a paraffinic gas oil or kerosine, at points further along in the coil so that the release of free radicals or reactive fragments is more evenly distributed throughout the reactant stream. When more than one sensitizer is employed, the total quantity of sensitizer should still preferably be within the range of 1 to 10 per cent by weight of the feed. When separate heating and soaking or reaction zones are employed in the pyrolysis coil of a

polymerization process for the conversion of C_2 to C_5 hydrocarbons to gasoline, the sensitizer may also be injected at various points in the coil. To supply free radicals or reactive fragments to the reaction zone the sensitizer may be injected at the beginning of the soaking or reaction coil or at a plurality of points along this coil. It is also possible to obtain an added advantage in a polymerization process of this type by introducing the sensitizer into the heating section of the pyrolysis coil. In this way, increased yields of olefins for polymerization can be obtained due to the presence of free radicals in the heating coil.

It is to be understood that the reaction conditions and methods of operation set forth in the specific examples recited herein are included by way of illustration only and are not to be construed limitations upon the present invention. The UOP characterization factor is defined as the ratio of the cube root of the molal average boiling point, in degrees Rankine, to the specific gravity of the hydrocarbon material. The characterization factor is a well-known quantitative expression for variations in physical properties with change in the character of the hydrocarbon stock. It is also to be emphasized that the theory set forth herein to explain this invention should not be construed as a limitation, but that the invention described is to be limited only by the appended claims.

Having described and illustrated our invention, what is claimed and is sought to be protected by Letters Patent is:

1. In a process for the thermal conversion of normally gaseous hydrocarbons at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur, the improvement comprising conducting said conversion in the presence of 1 to 10 per cent by weight of a predominantly paraffinic non-refractory hydrocarbon material having at least 7 carbon atoms per molecule.

2. In a process for the thermal conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur, the improvement comprising conducting said conversion in the presence of 1 to 10 per cent by weight of a predominantly paraffinic non-refractory hydrocarbon material having at least 7 carbon atoms per molecule.

3. In a process for the thermal conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce gaseous olefinic hydrocarbons, the improvement comprising carrying out said conversion in the presence of 1 to 10 per cent by weight of a predominantly paraffinic non-refractory hydrocarbon material having at least 7 carbon atoms per molecule.

4. In a process for cracking hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce gaseous olefinic hydrocarbons, the improvement comprising carrying out said cracking in the presence of 1 to 10 per cent by weight of a predominantly paraffinic non-refractory hydrocarbon material having at least 7 carbon atoms per molecule.

5. In a process for the dehydrogenation of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce gaseous olefinic hydrocarbons, the improvement comprising carrying out said dehydrogenation in the presence of 1 to 10 per cent by weight of a predominantly paraffinic non-refractory hydrocarbon material having at least 7 carbon atoms per molecule.

6. In a process for the thermal conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce liquid hydrocarbons boiling in the gasoline range, the improvement comprising carrying out said conversion in the presence of 1 to 10 per cent by weight of a predominantly paraffinic non-refractory hydrocarbon material having at least 7 carbon atoms per molecule.

7. In a process for the polymerization of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce liquid hydrocarbons boiling in the gasoline range, the improvement comprising carrying out said polymerization in the presence of 1 to 10 per cent by weight of a predominantly paraffinic non-refractory hydrocarbon material having at least 7 carbon atoms per molecule.

8. In a process for the thermal conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce gaseous olefinic hydrocarbons, the improvement comprising carrying out said conversion in the presence of 1 to 10 per cent by weight of a non-refractory hydrocarbon material having a UOP characterization factor of at least 12 and an aniline point of at least 150° F.

9. In a process for cracking hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce gaseous olefinic hydrocarbons, the improvement comprising carrying out said cracking in the presence of 1 to 10 per cent by weight of a non-refractory hydrocarbon material having a UOP characterization factor of at least 12 and an aniline point of at least 150° F.

10. In a process for the dehydrogenation of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce gaseous olefinic hydrocarbons, the improvement comprising carrying out said dehydrogenation in the presence of 1 to 10 per cent by weight of a non-refractory hydrocarbon material having a UOP characterization factor of at least 12 and an aniline point of at least 150° F.

11. In a process for the thermal conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce liquid hydrocarbons boiling in the gasoline range, the improvement comprising carrying out said conversion in the presence of 1 to 10 per cent by weight of a non-refractory hydrocarbon material having a UOP characterization factor of at least 12 and an aniline point of at least 150° F.

12. In a process for the polymerization of hydrocarbons having from 2 to 5 carbon atoms per molecule at elevated temperatures wherein cracking, dehydrogenation and polymerization reactions occur to produce liquid hydrocarbons boiling in the gasoline range, the improvement comprising carrying out said polymerization in the presence of 1 to 10 per cent by weight of a non-refractory hydrocarbon material having a UOP characterization factor of at least 12 and an aniline point of at least 150° F.

13. In a process for the thermal conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule wherein said hydrocarbons are heated to a temperature of 1400° to 1500° F. for a period of 0.7 to 1.3 seconds while maintaining a pressure of 10 to 30 pounds per square inch gauge, the improvement comprising carrying out said conversion in the presence of 1 to 10 per cent by weight of soft wax.

14. In a process for the thermal conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule wherein said hydrocarbons are heated to a temperature of about 1480° F. for a period of about 1 second while maintaining an average pressure of about 14 pounds per square inch gauge, the improvement comprising carrying out said conversion in the presence of from 1 to 10 per cent by weight of soft petroleum wax.

15. In a process for the conversion of hydrocarbons

having from 2 to 5 carbon atoms per molecule wherein said hydrocarbons are heated to a temperature of 900° to 1150° F. for a period of at least 1 minute while maintaining a pressure of about 60 to 3000 pounds per square inch gauge, the improvement comprising carrying out said conversion in the presence of 1 to 10 per cent by weight of soft petroleum wax.

16. In a process for the conversion of hydrocarbons having from 2 to 5 carbon atoms per molecule wherein said hydrocarbons are heated to a temperature of about 1050° to 1100° F. for a period of about 1 minute while maintaining a pressure of about 1200 pounds per square inch gauge, the improvement comprising carrying out said conversion in the presence of 1 to 10 per cent by weight of soft petroleum wax.

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