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PROCESS FOR DEHYDROGENATION OF PROPANE

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ABSTRACT OF THE DISCLOSURE

A process for dehydrogenating propane to provide higher selectivity to propylene by incorporating into the propane stream during dehydrogenation from about 2 to about 40 weight percent of H_2S or a compound which produces H_2S in situ.

This invention relates to an improved process for dehydrogenating propane to olefins and more particularly relates to a process for the thermal dehydrogenation of propane in the presence of H_2S as a diluent to provide an improved selectivity to propylene.

In the early days of the thermal modification of hydrocarbons, both dehydrogenation and cracking of the hydrocarbons were achieved but efforts were strongly directed to cracking or cleaving of the carbon-to-carbon bonds to produce either ethylene or aromatic hydrocarbons such as benzene. In such processes relatively small amounts of hydrogen sulfide (or other sulfur-containing compounds) were occasionally employed to reduce the carbon formation or to act as a sensitizer or promoter for the cracking reaction. For example, U.S. 2,168,840 shows the use of H_2S either in admixture with the hydrocarbon stream to be cracked or as a treatment for the inner surface of the reactor. In both instances, carbon formation is substantially prevented and in a substantial amount of aromatic hydrocarbons is produced. U.S. 2,415,477 shows the use of H_2S and other sulfur-containing compounds to accelerate the cracking of hydrocarbons by promoting the cleavage of the carbon-to-carbon bonds rather than that of the carbon-to-hydrogen bond.

In more recent times, when it was desired to maximize olefin production, it has been commercial practice that a diluent such as steam was employed. Most present day processes for the thermal dehydrogenation and cracking of hydrocarbons such as propane, therefore, employ steam as a diluent and produce more ethylene and propylene, less methane and only very small proportions of aromatics such as benzene. For example, the pyrolysis of propane in the presence of steam typically achieves a maximum single pass yield of propylene (usually 16–18%) at a conversion of about 65% and at this conversion usually produces about 25% ethylene, about 15% methane and about 3% heavier by-product, including cyclic aliphatic and aromatics. It is generally accepted that at higher conversions of propane, lower yields of propylene and higher yields of ethylene, methane and aromatics are produced. In practice the reaction is run at approximately 90% conversion.

Therefore, while it is frequently desirable to produce an olefin product containing a relatively high proportion of propylene with regard to ethylene at relatively high conversions of propane, this has not been possible to achieve with the presently available process employing steam as a diluent.

For the purposes of this invention, selectivity is defined as the weight of product produced per 100 weight of feed (propane) converted. It is sometimes also called ultimate yield.

Productivity is defined as the weight of a product produced per 100 weight of feed (propane).

It is an object of this invention to provide an improved process for the dehydrogenation of propane feeds to produce olefins. A further object is to provide a process wherein a higher ratio of propylene to ethylene is produced in the thermal dehydrogenation of propane. A still further object is to provide a process whereby higher conversions of the propane may be employed without unduly increasing the amount of cracking. These and other objects and advantages of the present process will become apparent from the following detailed description.

It has now been discovered that a yield of olefins and higher proportion of propylene to ethylene are achieved at high conversions if a propane feed containing from about 2 to about 40 weight percent of H_2S or an H_2S forming compound (calculated as H_2S) is passed through a thermal dehydrogenation zone having a temperature between about 650° C. and about 900° C. for a residence time of between 0.1 and about 3.0 seconds and the gases from such zone are passed to a quenching zone. For example, in the pyrolysis of propane, the use of 10 weight percent H_2S as the diluent in the place of steam will produce a propylene productivity of 30% at a propane conversion of 90%. While the mechanism is not completely established, it has been shown that H_2S, when employed as a diluent in the proper concentration and under the conditions of this invention, promotes the dehydrogenation reaction and thus relatively more propylene is produced than in the prior art.

It is highly advantageous in the present invention to employ high single pass conversions of the propane. Not only do high per pass conversions reduce or eliminate the need to recycle propane to the reactor but the productivity for olefins, i.e. ethylene and propylene, also increases up to conversions of about 90% for increasing levels of H_2S. It is desirable therefore to operate the process at conversions of at least about 70% with conversions between about 75 and about 95% being generally preferred.

In order to achieve the advantages of the present invention, it is necessary that the propane stream to be dehydrogenated contain, as a diluent, from about 2 to about 40 weight percent of H_2S, preferably from about 4 to about 15 weight percent of H_2S, during the pyrolysis. It is usually advantageous to admix the hydrogen sulfide with the propane feed before the temperature of the propane stream is above about 550° C. While gaseous H_2S is usually the preferred additive to the hydrocarbon feed, any sulfur-containing material (such as a mercaptan, or an alkyl sulfide or disulfide) may be employed which will form H_2S under the conditions of the dehydrogenation reaction.

Thermal dehydrogenation of the saturated propane feed is conducted at a temperature of between about 650° C. and about 900° C., preferably between about 725° C. and about 850° C. At temperatures below about 650° C., little dehydrogenation occurs even at excessively long contact times. At temperatures above about 900° C. excessive cracking occurs even at very short contact times.

The reaction is preferably conducted at or near atmospheric pressure as reaction pressures above about 30 p.s.i.g. are detrimental to the dehydrogenation reaction.

While the contact time at dehydrogenation temperature varies with the specific temperature employed and the degree of conversion desired, a contact or residence time in the pyrolysis zone of from about 0.1 to about 3 seconds is usually employed with from about 0.3 to about 1.5 seconds being generally preferred.

It is usually desirable from a practical standpoint to preheat the propane feed and the H_2S diluent prior to passing these materials to the dehydrogenation zone. In general, these feed materials are preheated to a temperature just below the temperature required for dehydrogena-

tion, e.g. a suitable preheat temperature is between about 550 and 600° C.

After passing from the pyrolysis zone where the dehydrogenation of the propane takes place, the product gases are rapidly quenched by passing them to a quench zone provided with a means for removing heat from such gases. This zone may be externally cooled by passing water or other fluid over the other surface or it may be internally cooled by such means as liquid sprays. While the particular means employed is not critical to the process of this invention, it is necessary that the product gases from the pyrolysis zone be quenched to prevent excessive cracking and the formation of undesirable by-products such as hydrogen methane, higher olefins and aromatics.

From the quench zone, the dehydrogenated product may be separated and appropriate components are recycled to the pyrolysis zone if desired.

The process of this invention therefore is carried out by admixing the feed stream containing propane with sufficient H_2S or H_2S-forming compound to serve as a diluent, heating the mixture to a temperature of between about 650 and about 900° C. for a time sufficient to dehydrogenate the desired proportion of the hydrocarbon feed and quenching the product gases.

The following examples are provided to further illustrate the invention but are not to be construed as limiting to the scope thereof.

EXAMPLE 1

A propane stream (99 mole percent) was fed at the rate of 225 cc./min. (at ambient conditions) to a preheater having a temperature of 599° C. Just prior to entering the preheater, a flow of 36 cubic centimeters per minute at ambient conditions of H_2S (11.0 weight percent of total feed) was introduced into the propane stream. The mixed stream of propane and H_2S passed through the preheater and to the thermal dehydrogenation reactor. The reactor was a tube of 304 stainless steel, 76 inches long, having an 0.12 inch inside diameter, and formed into a helical coil 28 inches in length. This coiled reactor was heated in a furnace. The upper inlet end of the reactor had a temperature of 815° C. and the lower exit end of the tube had a temperature of 775° C. After a residence time in the reactor of 0.7 second, the hot product gases passed immediately to a single tube heat exchanger cooled with room temperature water and which served as a quench. The pressure differential across the reactor was at all times two p.s.i. or less.

As the quenched effluent gases passed from the reactor system, the volume was measured, the gases were scrubbed to remove the H_2S therefrom. A small side stream was removed and passed to a gas chromatograph for determination of H_2 and hydrocarbon content. Analysis of the reactor off-gas showed an H_2S content of 10 weight percent and analysis of the gases after scrubbing with NaOH showed the following composition:

Component:	Wt. percent produced based on propane fed
H_2	0.84
CO, air	1.43
CH_4	19.93
C_2H_4	30.43
C_2H_6	4.44
C_3H_6	29.38
C_3H_8	8.13
Total	96.9

A small amount of heavier material (about 3%) was recovered and was composed chiefly of butadiene, butylenes, cyclopentadiene, benzene, toluene and isoprene.

EXAMPLES 2–19

In order to demonstrate the effect of H_2S concentration on propylene productivity at various levels of propane conversion, a series of runs were made using similar equipment and following the procedure of Example 1. The results based on a single pass are summarized in Table I below wherein all percentages are weight percent.

TABLE I

Example	Reactor	Percent of— H_2S	Propane conversion	Propylene yield	Productivity ethylene plus propylene	Residence time in seconds	Temp., ° C.
2	Stainless steel tube 0.125 in. I.D. 6' long	2	62	22	43	1.0	725
3	do	2	70	24	49	1.0	750
4	do	2	78	24	54	0.9	775
5	do	2	81	24	56	0.9	800
6	do	2	88	22	57	0.9	850
7	do	4	73	26	51	1.0	725
8	do	4	80	26	53	0.9	750
9	do	4	83	26	54	0.9	775
10	do	4	87	26	58	0.9	800
11	do	4	90	25	59	0.9	825
12	do	4	92	25	59	0.9	840
13	do	4	93	26	60	0.9	850
14	do	10	58	22	42	1.0	725
15	do	10	77	26	53	0.9	750
16	do	10	85	31	60	0.9	775
17	do	10	88	32	63	0.9	800
18	do	10	90-91	31	64	0.9	815
19	do	10	92	30	64	0.9	825
Control 1	Stainless steel tube 0.875 inch I.D. 1' long	0	61	17	42	1.0	725
Control 2	do	0	65	18	43	1.0	750
Control 3	do	0	71	18	47	1.0	775
Control 4	do	0	78	17	48	0.9	800
Control 5	do	0	86	16	49	0.9	825

NOTE.—Larger diameter reactor tube was used since a smaller diameter reactor tube rapidly became plugged with carbon when no H_2S was used.

EXAMPLE 20

In order to further illustrate the invention and compare the effects of steam and nitrogen diluents, the following data is presented.

The procedure of Example 1 was followed at high conversions using a straight 0.21 I.D. stainless steel tube six feet long, 11% H_2S in the propane feed with a 0.9–1.0 second residence time.

As a control, a similar process was run using the maximum amount of steam as a diluent with high conversions.

As a second control, data is presented from the litera-

ture showing the use of nitrogen as a diluent. The data is presented in Table II.

TABLE II

[Selectivities (wt. per 100 wt. converted) data interpolated from product distribution curves]

Percent propane conversion	11% H_2S (Ex. 20)		32% steam [1]		N_2 [2]	
	C_2H_4	C_3H_6	C_2H_4	C_3H_6	C_2H_4	C_3H_6
70	33	36	40	25	39	25
75	33	35	41	23	39	22
80	33	34	42	21	40	18
85	32	33	44	19	41	15
90	32	31	N.A.	N.A.	41	12

[1] 1.0" I.D. stainless steel tube, temperature 740-780° C., 15 p.s.i.g., steam/propane ratio 0.45.
[2] Data taken from Benkins et al. Ind. and Engr. Chemistry, Process Design and Development, July 1968, vol. 7, #3, pp. 435-442.

Improved results similar to the above examples are obtained with propane feeds having a lower percentage of propane. The propane feedstock should contain at least 50 mole percent propane.

We claim:

1. A process for the thermal dehydrogenation of a propane feed to olefins which comprises admixing a propane feed with from about 2 to about 40 weight percent of H_2S, heating such mixture in a dehydrogenation zone to a temperature of between about 650° C. to about 900° C. for a residence time of between about 0.1 and about 3 seconds, and passing the gas mixture from the dehydrogenation zone to a quench zone wherein the gases are cooled to a temperature below about 600° C.

2. A process for the thermal dehydrogenation of a propane feed to olefins as set forth in claim 1 which consists essentially of admixing a propane feed with from about 4 to about 15 weight percent H_2S.

3. The process of claim 1 wherein the dehydrogenation temperature is between about 725 and about 850° C.

4. The process of claim 1 wherein the propane is preheated to a temperature of between about 550 and about 600° C. prior to passing to the dehydrogenation zone.

5. The process of claim 1 wherein the contact time in the dehydrogenation zone is between about 0.3 and about 1.5 seconds.

6. The process of claim 1 wherein the contact time and dehydrogenation temperature as defined in claim 1 are selected to produce a conversion of propane of at least 70 weight percent.

7. The process of claim 6 wherein the conversion of propane is between about 75 and about 95 weight percent.

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