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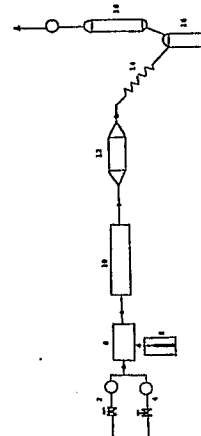
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54 **Process for up-grading steam-cracking products.**

57 There is provided with the present invention a new process for up-grading products resulting from the steam-cracking of hydrocarbons which comprises bringing the steam-cracking reaction products in contact with a catalyst comprising a mixture of from 2.5 to 7.5% wt of Cr_2O_3 , 5 to 17.5% wt of Al_2O_3 and 75 to 85% wt of a Zn-ZSM-5 zeolite or a Zn-ZSM-5 zeolite/asbestos and recovering the desired products.

FIGURE 11 SCHEMATIC DIAGRAM OF THE PROCESS FOR UP-GRADING PRODUCTS RESULTING FROM THE STEAM-CRACKING OF HYDROCARBONS



Description

PROCESS FOR UP-GRADING STEAM-CRACKING PRODUCTS

BACKGROUND OF THE INVENTION

5 Steam-cracking is one of the most widely used basic petrochemical processes. It is used by industries to produce light olefins such as ethylene, propylene, butenes and butadiene and it is also relied upon for the production of aromatics such as benzene, toluene and xylenes.

Basically, steam-cracking comprises a step in which the hydrocarbon mixture to be transformed is mixed with steam and submitted to elevated temperatures in a tubular reactor. The different resulting products, 10 gaseous and liquid hydrocarbons are then collected and separated. Thus, product distribution depends on the nature of the initial hydrocarbon mixture as well as experimental conditions.

Among the products obtained, C₂-C₄ light olefins, as well as benzene, toluene, ethylbenzene and xylenes have the highest commercial values and since enormous quantities are processed throughout the world, even small yield improvements lead to substantial profit increases.

15 In recent years, ZSM-5 zeolite catalysts have drawn considerable attention because of their ability to increase selectivity in a variety of industrial processes such as xylene isomerization, toluene disproportionation, aromatic alkylation and methanol conversion.

It has been shown that the zeolite's selectivity properties are the result of its tridimensional channel network and of the different pore sizes of its structure.

20 One of the most interesting areas where ZSM-5 zeolites have shown substantial catalytic activity is in the process in which methanol is converted into hydrocarbons. Thus, by using appropriate reaction conditions, very high yields in C₅-C₁₁ gasoline hydrocarbons can be obtained. However, this reaction presents the drawback of producing small quantities of durene, an undesirable reaction product.

Furthermore, modifications of the catalyst can also lead to highly efficient production of light olefins 25 resulting from methanol conversion.

Thus, it can be seen that modified zeolite catalysts have the possibilities to present very interesting properties for enhancing yields in petrochemical reactions.

Therefore, since steam-cracking is one of the most widespread petrochemical processes, it would be highly desirable to provide means for increasing production of the most valuable reaction products.

SUMMARY OF THE INVENTION

The present invention relates to a process for up-grading products resulting from the steam-cracking of hydrocarbons which comprises bringing the steam-cracking reaction products in contact with a multifunctional Zn-ZSM-5 zeolite/Cr₂O₃/Al₂O₃ catalyst comprising of a mixture of from 2.5 to 7.5% wt of 30 Cr₂O₃, 5 to 17.5% wt of Al₂O₃ and 75 to 85% wt of a Zn-ZSM-5 zeolite or a Zn-ZSM-5 zeolite/asbestos. Such a process allows for significant yield increases in C₂-C₄ olefins. Furthermore, the commonly obtained pyrolysis oil is up-graded to a high grade gasoline, rich in mono-aromatics and free from undesirable durennes and long aliphatic chains.

DETAILED DESCRIPTION OF THE INVENTION

40 The main feature of the present invention resides in the presence of a catalytic reactor at the outlet of the steam-cracking reactor. This catalytic reactor contains a multifunctional catalyst which comprises a zeolite of the ZSM-5 type coupled with metallic oxides.

These oxides can either be coupled to the zeolite by being directly deposited on the zeolite or mechanically 45 mixed with the zeolite.

The metallic oxides can be selected from oxides such as Cr₂O₃, Al₂O₃, or from any metallic oxide having a hydrogenating/dehydrogenating function.

In the case of the Cr₂O₃/Al₂O₃ proportions of Cr₂O₃ ranging between 2.5 and 7.5% wt, proportions of Al₂O₃ 50 ranging between 5 and 17.5% wt and proportions of the zeolite catalyst ranging between 75 and 85% wt can be used.

Although the catalytic reactor used in the present invention was a fixed-bed reactor, it will be understood that any suitable design commonly used for catalytic reactions could have been chosen.

In the drawings:

Figure 1 represents a schematic drawing of the bench scale setting for the catalytic up-grading of 55 products resulting from the steam-cracking of hydrocarbons.

Figure 2 represents a comparison between the amounts of C₂-C₄ olefins obtained by steam-cracking alone and by steam-cracking along with various zeolite catalysts.

Figure 3 represents a comparison between the amounts of ethylene obtained by steam-cracking alone and by steam-cracking along with various zeolite catalysts.

60 Referring now to Figure 1, the starting hydro-carbon material 2 is first mixed with a stripping gas 4. It is to be noted, however, that the use of a stripping gas is optional. In the context of the actual experiments, a stripping gas was used only for convenience.

The resulting mixture is then forwarded to a vaporizer-mixer 6, in which steam is injected by means of an

infusion pump 8. The gaseous mixture thus obtained enters a steam-cracking tubular reactor 10 heated at a temperature ranging between 760° and 860° C. In a further step, products coming out of the steam-cracking tubular reactor 10 are sent into a catalytic reactor 12 heated at a temperature ranging between 450° and 550° C. The resulting products are then cooled by a series of condensers 14 (water-cooling condensers and ice bath). Immediately following the cooling step, the liquid and gaseous phases are separated. The liquids are first collected in a liquid-collector cylinder 16 while the gases flow through the liquid-collector cylinder to be collected for on line analysis in a dynamic sampler cylinder 18 located at a higher position than the liquid collector cylinder.

The present invention will be more readily understood by referring to the following examples which are given to illustrate rather than limit the scope of the invention.

EXAMPLE 1

Propane is the starting hydrocarbon material on which the steam-cracking process was performed. It was introduced into the system at a flow rate of 45 ml/min. or 4.95 g/hour. It was first mixed with helium acting as a stripping gas. After having been flown through the vaporizer-mixer, in which steam was injected at a rate of 1.7 g/hour, the gaseous mixture was then sent into the steam-cracking reactor whose internal temperature had been set to 780° C at atmospheric pressure. The residence time of the starting material in the steam-cracking reactor was approximately 1 second.

The resulting product was then separated into its liquid and the gaseous phases. The liquid fraction was analyzed by GC using a capillary column (length: 50 m, PONA® type, fused silica coated with a cross-linked polymer). The gases were analyzed on line by gas chromatography. A column having a length of 3.5 m packed with Chromosorb® P coated with 20% by weight of Squalane® was used for the analysis. The GC used was a dual FID Hewlett-Packard Model 5790 equipped with a 3392A Model integrator. Results are shown in Table 1.

EXAMPLE 2

The same procedure as in Example 1 was repeated the only modification being the internal temperature of the steam-cracking reactor which was set at 800° C. Results are shown in Table 1.

EXAMPLE 3

The same procedure as in Example 1 was repeated the only modification being the internal temperature of the steam-cracking reactor which was set at 835° C. Results are shown in Table 5.

EXAMPLE 4

As in Example 1 propane was chosen as the starting hydrocarbon material. It was mixed with helium and flown through the vaporizer-mixer. The gaseous mixture was then forwarded through the steam-cracking reactor whose internal temperature had been set to 780° C. The resulting products were then sent to the catalytic reactor which had been previously embedded with 4 g of a Zn-Mn-ZSM-5 zeolite which was prepared according to the procedure described in Can. Pat. Appl. S.N. 471,463 (US-A-4 615 995). The temperature of the catalytic reactor had been previously set at 500° C, with a pressure of 1 atmosphere and a W.H.S.V. (weight hourly space velocity) of 1 h⁻¹. The final products were analyzed using the techniques discussed in Example 1. Results are shown in Table 2.

EXAMPLE 5

The same procedure as in Example 4 was repeated, the only modification being the internal temperature of the steam-cracking reactor which was set at 800° C. Results are shown in Table 2.

EXAMPLE 6

The same procedure as in Example 4 was repeated, except for the following modifications: the catalytic reactor was embedded with 4 g of a Zn-Mn-ZSM-5 zeolite/asbestos catalyst prepared according to the procedure described in Can. Pat. Appl. S.N. 471,463 (US-A-4 615 995). Results are shown in Table 3.

EXAMPLE 7

The same procedure as in Example 6 was repeated, the only modification being the internal temperature of the steam-cracking reactor which was set at 800° C. Results are shown in Table 3.

EXAMPLE 8

The same procedure as in Example 4 was repeated, except for the following modification: the catalytic reactor was embedded with a Zn-ZSM-5 zeolite/asbestos/Cr₂O₃/Al₂O₃ catalyst. The Zn-ZSM-5 zeolite/asbestos catalyst was prepared according to the method described in Can. Pat. Appl. S.N. 471,463. Then, 4.5 g of the Zn-ZSM-5 zeolite/asbestos catalyst obtained were wet with a solution prepared from 0.3 g of Cr₂O₃ and 0.4 g of sodium aluminate dissolved in 5 ml of distilled water. The resulting multifunctional catalyst was dried at 120° C for 12 hours and actuated at 500° C for another 12 hour period. Finally, the catalyst was reduced in hydrogen at 350° C for at least 1 hour. Results are shown in Table 4.

EXAMPLE 9

The same procedure as in Example 8 was repeated, the only modification being the internal temperature of the steam-cracking reactor which was set at 800°C. Results were shown in Table 4.

When studying the results obtained from the various examples, it is to be noted that in the steam-cracking process alone (Table 1) significant increases in highly valuable compounds such as ethylene, benzene and toluene are observed when the internal temperature of the reactor is increased from 780° to 800°C. The amount of less valuable products such as methane is higher at 800°C but this increase is compensated by a decrease in C₂-C₄ paraffins.

As for the aromatic content, there is a dramatic decrease in less valuable C₅-C₁₁ aliphatics, resulting in the obtention of more interesting products such as benzene, xylenes and toluene. In examples 4 to 7, Zn-Mn-ZSM-5 zeolite and Zn-Mn-ZSM-5 zeolite/asbestos, two known catalysts were used to form the catalytic bed. As it can be seen in Tables 2 and 3, and in Figures 2 and 3, inferior results were obtained when compared to steam-cracking alone as far as the olefin content is concerned, regardless of the temperature at which the reactions were performed.

As for the aromatic content, better results were obtained, but these results are at the best sufficient and no more, to compensate the quality loss on the side of the olefin production, especially, as far as ethylene is concerned, since ethylene is the most valuable steam-cracking product.

Thus, in the light of these results, one could tend to be led away from using zeolite catalysts as means to improve steam-cracking processes.

In Examples 8 and 9, the results obtained by using a multifunctional catalyst point out better results in both olefin and aromatic productions. Thus, it has been discovered as it can be seen in Figures 2 and 3, that the use of metal oxides co-catalyst coupled with a zeolite type catalyst unexpectedly increases the amounts of valuable steam-cracking products. In fact, the total amount of C₂-C₄ olefins and especially ethylene obtained by using the multifunctional catalyst after a steam-cracking reaction of 780° (55.8% wt) is even superior to the amount obtained when performing the steam-cracking reaction alone at 800° (47.1 wt).

Moreover as described in Example 3, a run without catalyst was performed at 835°C. This temperature was fairly close to temperatures used in industrial steam-cracking facilities using propane as a starting hydrocarbon material. When the product distribution of such a run is compared to the run performed in presence of the Zn-ZSM-5 zeolite/asbestos/Cr₂O₃/Al₂O₃ catalyst and with the steam-cracking reactor temperature set at 800°C, as described in Example 9, it can be seen, as it is shown in Table 5, that in the presence of the multifunctional catalyst and with a much lower steam-cracking temperature, higher yields in ethylene and propylene were obtained. The propylene yield was nearly doubled (due mainly to a lower steam-cracking temperature) and the ethylene yield was increased by 5 wt percentage points while methane formation was significantly lower.

Furthermore, the liquid yield was much lower for the run performed at a lower steam-cracking temperature in the presence of the multifunctional catalyst. However, the BTX aromatics (benzene, toluene, ethylbenzene and xylenes) content in the liquid hydrocarbon products was much higher and there was no formation of undesirable hydrocarbons.

Thus, by performing the steam-cracking of propane at a lower temperature and by using a multifunctional catalyst, the total "ethylene + propylene" yield can be increased by 10 wt percentage points and the ethylene/propylene wt ratio can be decreased to a very large extent (see Table 5).

From an industrial viewpoint, this would represent a real advantage since the present market trends are for a lower demand in ethylene and an increasing demand in propylene.

It will be appreciated that even though yields increase in valuable products ranging from 5 to 10% wt do not seem to be of significant importance, because of the enormous amounts of hydrocarbon material refined every day throughout the world, even a 0.5% wt yield increase represents millions of dollars of profits for petrochemical industries. Therefore, it is submitted that every invention increasing production yields in the petrochemical conversion processes has tremendous commercial values for these industries.

It will also be understood that although the process of the present invention has been developed for up-grading steam products, it can also be applied to every situation where starting materials such as pyrolysis oil, pyrolysis gasoline, mixtures of light olefins, light paraffins or mixture thereof are flown directly into the catalytic reactor without requiring any passage through a steam-cracking reactor.

In such cases, the multifunctional properties of the catalyst are expressed through several actions such as acid-catalyzed reactions (cracking, oligomerization, isomerization, transmutation) and redox reactions on intermediates leading to the final products or on the products themselves.

Therefore, in the framework of the present invention, the reactor containing the multifunctional catalyst can be located either after the steam-cracking reactor or after the liquid/gases separation operation (thus intercepting the liquid or gaseous products) and still obtain similar end results.

TABLE 1 DISTRIBUTION OF STEAM-CRACKING PRODUCTS OBTAINED IN THE ABSENCE OF CATALYST

Gaseous Products	Commercial Value	Reaction Temperature °C		Liquid Products	Commercial Value	Reaction Temperature °C	
		780 % wt Obtained	800 % wt Obtained			780 % wt Obtained	800 % wt Obtained
ETHYLENE	Highest ↓ Lowest	31.9	37.5	LIQUID YIELD (wt %)		2.2 (1)	2.9 (1)
PROPYLENE		11.8	10.9	BENZENE	Highest	0.0	0.4
(BUTENES + BUTADIENE)		3.4	3.5	XYLENES		0.0	0.1
(C ₂ +C ₄ PARAF-FINS)		16.3	11.6	ETHYL-BENZENE		0.0	0.0
PROPANE		16.7	10.7	TOLUENE		0.0	0.2
METHANE		17.7	22.9	C ₉ -C ₁₀ AROMATICS		0.0	0.5
TOTAL OLEFIN YIELD (wt %)		47.1	51.9	C ₅ -C ₁₁ ALIPHATICS	Lowest	2.2	1.7
PROPANE CONVERSION (wt %)		83.3	89.3	TOTAL AROMATIC CONTENT (Z)		0.0	42

(1) Presence of hydrocarbons heavier than C₁₁

TABLE 2: COMPARISON OF DISTRIBUTION OF STEAM-CRACKING PRODUCTS OBTAINED IN THE ABSENCE OF CATALYST AND IN THE PRESENCE OF Zn-Mn-ZSM-5 ZEOLITE CATALYST

Gaseous Products	Commer- cial Value	Steam-Cracking Temperature (°C)				Liquid Products	Commer- cial Value	Steam-Cracking Temperature (°C)			
		780 % wt obtained no catalyst	780 % wt obtained Zn-Mn-ZSM-5 catalyst	800 % wt obtained no catalyst	800 % wt obtained Zn-Mn-ZSM-5 catalyst			780 % wt obtained no catalyst	780 % wt obtained Zn-Mn-ZSM-5 catalyst	800 % wt obtained no catalyst	800 % wt obtained Zn-Mn-ZSM-5 catalyst
ETHYLENE	Highest ↓ Lowest	31.9	22.9	37.5	32.8	LIQUID YIELD (wt %)		2.2 (1)	7.1 (2)	2.9 (1)	6.8 (2)
PROPYLENE		11.8	12.1	10.9	10.7	BENZENE	Highest	0.0	0.7	0.4	0.7
(BUTENES + BUTADIENE)		3.4	8.7	3.5	6.3	XYLENES		0.0	0.9	0.1	0.8
(C ₂ +C ₄ PARAFFINS)		16.3	15.2	11.6	10.4	ETHYL-BENZENE		0.0	0.4	0.0	0.5
PROPANE		16.7	14.4	10.7	8.6	TOLUENE		0.0	1.0	0.2	1.2
METHANE		17.7	19.7	22.9	24.4	C ₉ -C ₁₀ AROMATICS		0.0	1.1	0.5	0.9
PROPANE CONVERSION (wt %)		83.3	85.6	89.3	91.4	C ₅ -C ₁₁ ALIPHATICS	Lowest	2.2	3.0	1.7	2.7
TOTAL OLEFIN YIELD (wt %)		47.1	43.7	51.9	49.8	TOTAL AROMATIC CONTENT (%)		0.0	58	42	61

(1) Presence of hydrocarbons heavier than C₁₁ (2) Absence of hydrocarbons heavier than C₁₁

TABLE 3 COMPARISON OF DISTRIBUTION OF STEAM-CRACKING PRODUCTS OBTAINED IN THE ABSENCE OF CATALYST AND IN THE PRESENCE OF Zn-Mn-ZSM-5 ZEOLITE/ASBESTOS CATALYST

Gaseous Products	Commercial Value	Steam-Cracking Temperature (°C)				Liquid Products	Commercial Value	Steam-Cracking Temperature (°C)			
		780 wt % obtained no catalyst	780 wt % obtained Zn-Mn-ZSM-5 zeolite/ asbestos catalyst	800 wt % obtained no catalyst	800 wt % obtained Zn-Mn-ZSM-5 zeolite/ asbestos catalyst			780 wt % obtained no catalyst	780 wt % obtained Zn-Mn-ZSM-5 zeolite/ asbestos catalyst	800 wt % obtained no catalyst	800 wt % obtained Zn-Mn-ZSM-5 zeolite/ asbestos catalyst
ETHYLENE	Highest	31.9	22.7	37.5	31.5	BENZENE	Highest	0.0	0.4	0.4	0.4
PROPYLENE	Lowest	11.8	11.6	10.9	11.3	XYLENES	Lowest	0.0	0.5	0.1	0.7
(BUTENES + BUTADIENE)		3.4	8.4	3.5	8.2	ETHYL-BENZENE		0.0	0.4	0.0	0.4
(C ₂ +C ₄ PARAFFINS)		16.3	16.5	11.6	10.3	TOLUENE		0.0	0.9	0.2	1.2
PROPANE	Lowest	16.7	16.8	10.7	8.3	C ₉ -C ₁₀ AROMATICS	Lowest	0.0	1.0	0.5	1.2
METHANE		17.7	18.4	22.9	23.8	C ₅ -C ₁₁ ALIPH.		2.2	2.5	1.7	2.8
PROPANE CONVERSION (wt %)		83.3	83.2	89.3	91.7	TOTAL AROMATIC CONTENT (Z)					
TOTAL OLEFIN YIELD (wt %)		47.1	42.7	51.9	51.0			0.0	56	42	58

(1) Presence of hydrocarbons heavier than C₁₁ (2) Absence of hydrocarbons heavier than C₁₁

TABLE 4: COMPARISON OF DISTRIBUTION OF STEAM-CRACKING PRODUCTS OBTAINED IN THE ABSENCE OF CATALYST
AND IN THE PRESENCE OF Zn-ZSM-5 ZEOLITE/ASBESTOS/Cr₂O₃/Al₂O₃ CATALYST

Gaseous Products	Commer- cial Value	Steam-Cracking Temperature (°C)				Liquid Products	Commer- cial Value	Steam-Cracking Temperature (°C)			
		780 wt obtained no catalyst	780 wt obtained Zn-ZSM-5 zeolite/ asbestos/ Cr ₂ O ₃ / Al ₂ O ₃ Catalyst	800 wt obtained no catalyst	800 wt obtained Zn-ZSM-5 zeolite/ asbestos/ Cr ₂ O ₃ / Al ₂ O ₃ Catalyst			780 wt obtained no catalyst	780 wt obtained Zn-ZSM-5 zeolite/ asbestos/ Cr ₂ O ₃ / Al ₂ O ₃ Catalyst	800 wt obtained no catalyst	800 wt obtained Zn-ZSM-5 zeolite/ asbestos/ Cr ₂ O ₃ / Al ₂ O ₃ Catalyst
ETHY- LENE	Highest	31.9	41.5	37.5	46.2	LIQUID YIELD (wt %)	2.2 (1)	2.2 (1)	2.1 (2)	2.9 (1)	3.1 (2)
PROPY- LENE		11.8	11.4	10.9	8.7	BENZENE	High- est	0.0	0.2	0.4	0.4
(BUTENES + BUTADIENE)		3.4	2.9	3.5	3.2	XYLENES		0.0	0.2	0.1	0.4
(C ₂ +C ₄ PARAFFINS)		16.3	10.5	11.6	6.9	ETHYL- BENZENE		0.0	0.1	0.0	0.3
PROPANE		16.7	8.2	10.7	4.0	TOLUENE		0.0	0.2		
METHANE	Lowest	17.7	23.4	22.9	27.9	C ₉ -C ₁₀ AROMA- TICS		0.0	0.6	0.2	0.7
PROPANE CONVERSION (wt %)		83.3	91.8	89.3	96.0	C ₅ -C ₁₁ ALIPH.	Low- est	2.2	0.8	1.7	0.8
TOTAL OLEFIN YIELD (wt %)		47.1	55.8	51.9	58.1	TOTAL AROMATIC CONTENT (%)		0.0	57	42	73

(1): Presence of hydrocarbons heavier than C₁₁ (2): Absence of hydrocarbons heavier than C₁₁

TABLE 5: COMPARISON OF DISTRIBUTION OF STEAM-CRACKING PRODUCTS OBTAINED IN THE ABSENCE OF CATALYST AT 835°C AND IN THE PRESENCE OF Zn-ZSM-5 ZEOLITE/ASBESTOS/Cr₂O₃/Al₂O₃ CATALYST AT 800°C

Gaseous Products	Commercial Value	Steam-Cracking Temperature (°C)		Liquid Products	Steam-Cracking Temperature (°C)	
		835 % wt obtained no catalyst	800 % wt obtained Zn-ZSM-5 zeolite/asbestos/ Cr ₂ O ₃ /Al ₂ O ₃ catalyst		835 % wt obtained no catalyst	800 % wt obtained Zn-ZSM-5 zeolite/asbestos/ Cr ₂ O ₃ /Al ₂ O ₃ catalyst
ETHYLENE	Highest ↓ Lowest	41.2	46.2	LIQUID HYDROCARBON YIELD (wt %)	7.8	3.1
PROPYLENE		4.5	8.7			
(BUTENES + BUTADIENE)		3.2	3.2	Total aromatic content (%) BTX aromatic content (%) Liquid hydrocarbons heavier than C ₁₁ (%)	78.4 48.3 4.0	73.1 58.2 0.0
(C ₂ +C ₄ PARAFFINS)		7.7	6.9			
PROPANE		6.1	4.0			
METHANE		29.5	27.9			
PROPANE CONVERSION (wt %)		93.9	96.0			
(ETHYLENE + PROPYLENE) YIELD (wt %)		45.7	54.9			
ETHYLENE/PROPYLENE wt ratio		9.2	5.3			

Claims

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1. A process for up-grading products resulting from the steam-cracking of hydrocarbons which comprises bringing the steam-cracking reaction products in contact with a catalyst comprising of mixture of from 2.5 to 7.5% wt of Cr_2O_3 , 5 to 17.5% wt of Al_2O_3 and 75 to 85% wt of a Zn-ZSM-5 zeolite or a Zn-ZSM-5 zeolite/asbestos and recovering the desired products.

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2. The process of Claim 1, wherein Cr_2O_3 and Al_2O_3 are directly deposited on the Zn-ZSM-5 zeolite or the Zn-ZSM-5 zeolite/asbestos.

3. The process of Claim 1, wherein Cr_2O_3 and Al_2O_3 are mechanically mixed with the Zn-ZSM-5 zeolite or the Zn-ZSM-5 zeolite/asbestos.

4. The process of Claim 1, wherein the catalyst is packed in a tubular reactor.

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5. The process of Claim 4, wherein the catalytic tubular reactor temperature is maintained between 400° and 600° C.

6. A catalyst suitable for up-grading products resulting from the steam-cracking of hydrocarbons, said catalyst comprising 2.5 to 7.5% wt of Cr_2O_3 , 5 to 17.5% wt of Al_2O_3 and 75 to 85% wt of a Zn-ZSM-5 zeolite or a Zn-ZSM-5 zeolite/asbestos.

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7. The catalyst of Claim 6, wherein Cr_2O_3 and Al_2O_3 are mechanically mixed with the Zn-ZSM-5 zeolite or the Zn-ZSM-5 zeolite/asbestos.

8. The catalyst of Claim 6, wherein Cr_2O_3 and Al_2O_3 are directly deposited on the Zn-ZSM-5 zeolite or the Zn-ZSM-5 zeolite/asbestos.

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9. A process for up-grading products resulting from the steam-cracking of hydrocarbons which comprises:

a) setting the steam-cracking reactor at a temperature lower by 30° C to 50° C than that normally used,

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b) bringing the steam-cracking reaction products in contact with a catalyst comprising of a mixture of from 2.5 to 7.5% wt of Cr_2O_3 , 5 to 17.5% wt of Al_2O_3 and 75 to 85% wt of a Zn-ZSM-5 zeolite or a Zn-ZSM-5 zeolite/asbestos and recovering the desired products.

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FIGURE 1: SCHEMATIC DRAWING OF THE PROCESS FOR UP-GRADING PRODUCTS RESULTING FROM THE STEAM-CRACKING OF HYDROCARBONS

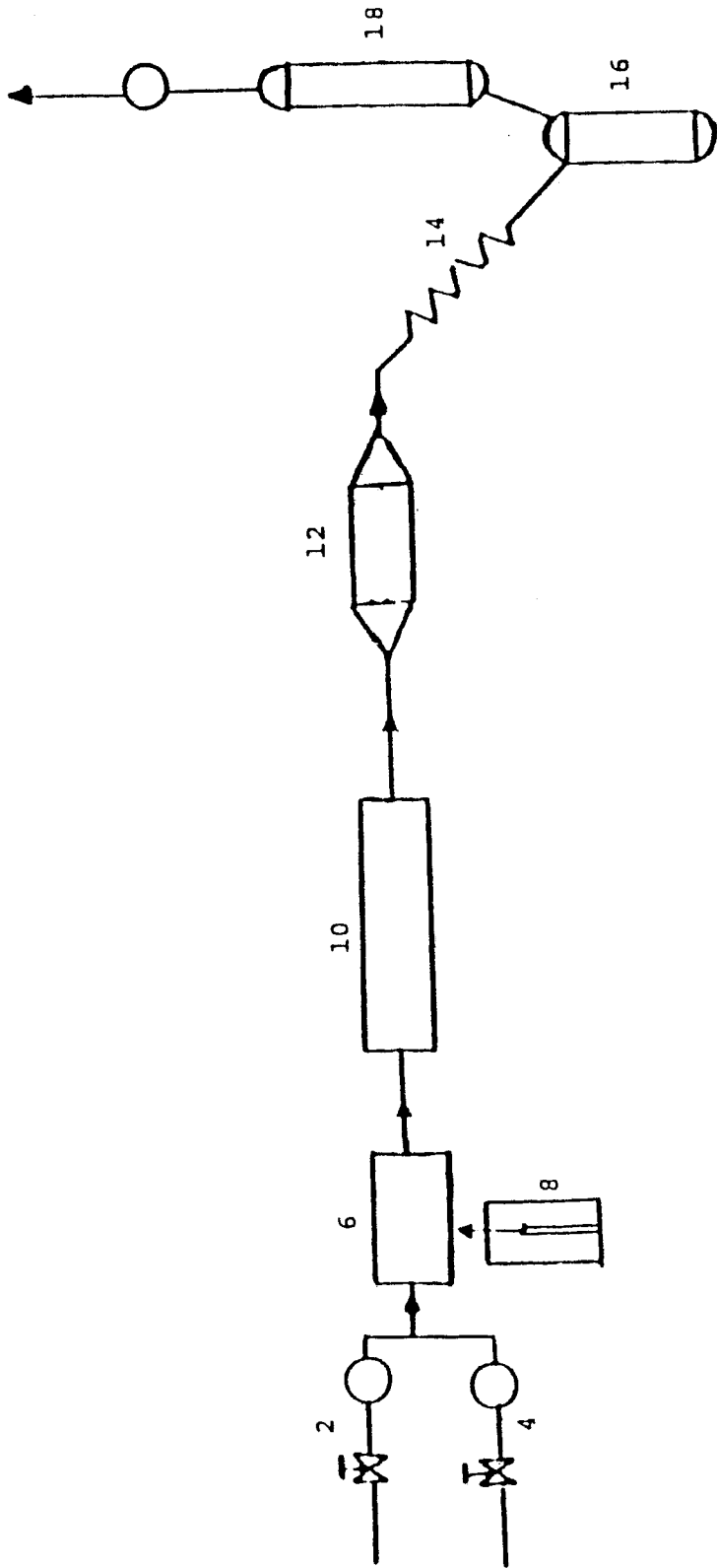
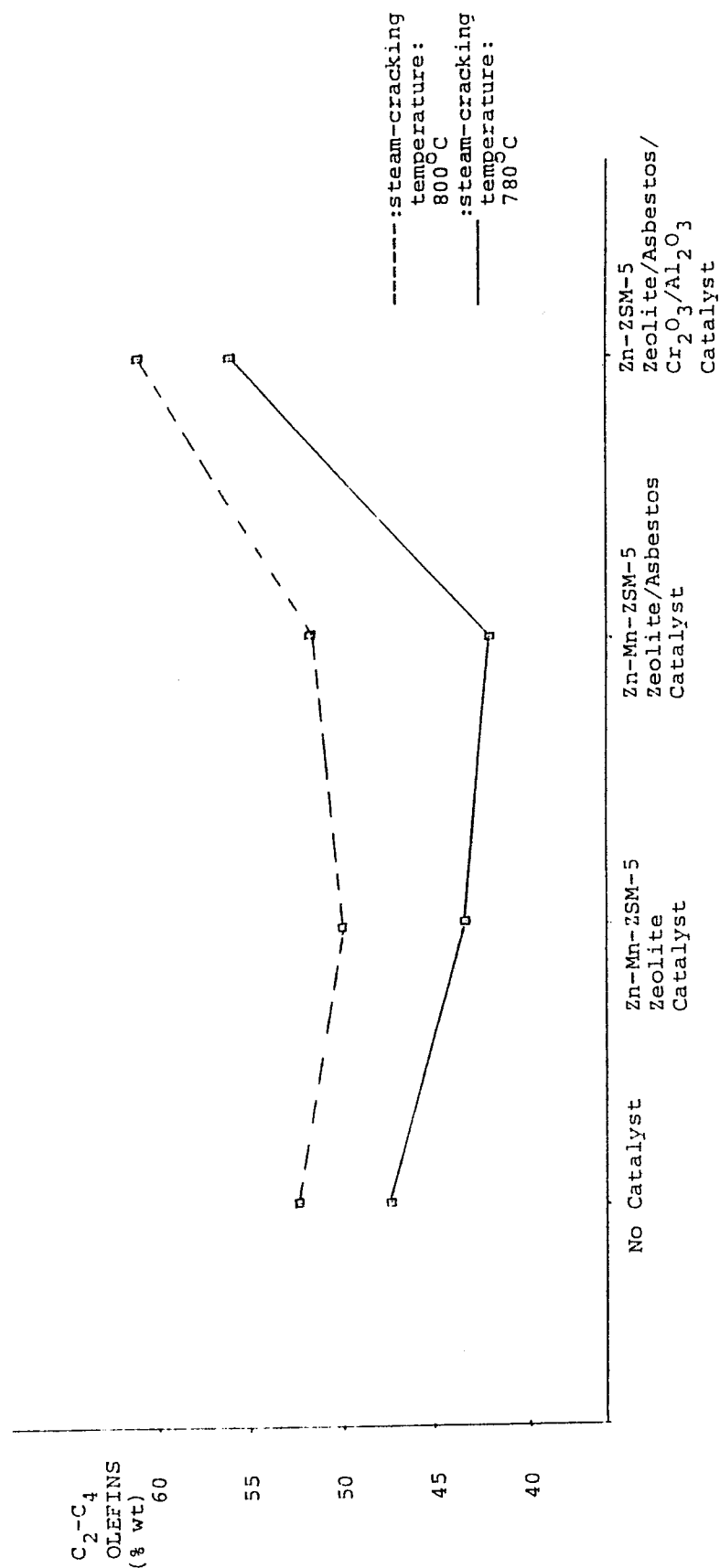


FIGURE 2: COMPARISON OF THE AMOUNTS OF C_2-C_4 OLEFINS OBTAINED BY STEAM-CRACKING ALONE AND BY STEAM-CRACKING ALONG WITH VARIOUS ZEOLITE CATALYSTS AT $780^\circ C$ AND $800^\circ C$.



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FIGURE 3: COMPARISON OF THE AMOUNTS OF ETHYLENE OBTAINED BY STEAM-CRACKING ALONE AND BY STEAM-CRACKING ALONG WITH VARIOUS ZEOLITE CATALYSTS AT 780°C AND 800°C

