

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **83200611.8**

(51) Int. Cl.³: **C 10 G 35/06**
C 10 G 45/68

(22) Date of filing: **29.04.83**

(30) Priority: **30.04.82 US 373729**

(43) Date of publication of application:
09.11.83 Bulletin 83/45

(84) Designated Contracting States:
BE DE FR GB IT NL SE

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(54) **Conversion of certain hydrocarbons using calcined TEA silicate catalyst.**

(57) By-product effluent streams from pyrolytic hydrocarbon cracking processes, containing monoolefins and diolefins, are treated to hydrogenate the olefins and to aromatize the aliphatics, with a catalyst essentially comprising a calcined TEA-silicate.

CONVERSION OF CERTAIN HYDROCARBONS USING
CALCINED TEA-SILICATE CATALYST

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related to two patent applications
filed concurrently herewith (attorney's docket nos.
Eur 1235 & Eur 1236).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the preparation of streams
containing recoverable benzene, toluene, and xylenes ("BTX")
from initial by-product effluent streams that contain other com-
ponents, notably monoolefins and diolefins. In one aspect, the
invention concerns the removal by conversion of these other
components which ordinarily prevent recovery by distillation
or solvent extraction of benzene-toluene-xylenes aromatics from
the streams. In another aspect, it concerns a low severity
process for treating the by-product streams with a specified
catalyst, and under defined reaction conditions, both to pro-
duce benzene-toluene-xylenes from the initial stream and to
reduce or eliminate those components that otherwise would in-
terfere with the economic recovery of these aromatics from
the streams.

2. Description of Prior Art

The preparation of light olefins and diolefins,
mainly ethylene, propylene, and butadiene, by the thermal
pyrolysis, or cracking, of petroleum fractions is well known
and widely practiced. (See for example, Kirk & Othmer's
"Encyclopedia of Chemical Technology", Second Edition, Vol. 8,
pp. 503-514.) In these pyrolytic cracking processes, hydro-

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carbons ranging from ethane, through LPG (liquefied petroleum gas, chiefly propane with a few percent butanes), naphtha, heavy gas oil, to even crude petroleum oil, are subjected to high temperature conditions, at low pressure and for a short time, to produce a maximum of the desired product. These thermal processes vary widely, and the yields from any one process depend not only on process equipment and conditions, but on such extraneous factors as the presence or absence of diluents and other reactants, e.g., oxygen, hydrogen, steam, etc.

Even the best of the pyrolytic processes is less than ideally selective. As a consequence, the total reactor effluent will contain not only the desired olefin or diolefin, but a variety of other components, ranging from methane gas to high boiling polycyclic hydrocarbons. These by-products are conventionally separated, usually by distillation and/or absorption, so as to concentrate the main desired products for ultimate recovery, and to produce one or more by-product effluent streams.

The by-product effluents contain a mixture of hydrocarbon types, including paraffins, monoolefins, diolefins, aromatics, cyclics, and various substituted and polynuclear aromatics. Unless the by-product effluent stream or streams contains a particularly valuable or desirable component, making removal economical, the by-product effluent streams are of only limited utility. The lighter gases are useful only as fuel, while the heavier, normally liquid, components usually termed "dripolene," if not hydrogenated and then subjected to BTX extraction, are customarily either burned locally as fuel or else hydrogenated to saturate the unstable diolefins, and then blended with other gasoline fractions as motor fuel.

It has long been recognized that some of these by-product effluent streams, particularly the dripolene fractions, contain potentially valuable benzene, toluene, and xylenes (including ethylbenzene). Unfortunately, they also contain diolefins and monoolefins, which effectively interfere with most existing solvent extraction processes, such as the Udex and Sulfolane processes, for the extraction of aromatics from paraffins. Some of these olefins have boiling points similar to those of the BTX aromatics, and hence cannot be removed by fractional distillation. Selective hydrogenation to saturate the olefins and diolefins is practiced, and widely so, but the process tends to be expensive. Moreover, the diolefins in dripolene tend to be thermally unstable, forming catalyst-deactivating and exchanger-fouling carbonaceous deposits.

A variety of catalysts has been proposed for treating one or more of the by-product effluents from pyrolytic cracking processes so as to render the streams more valuable or more amenable to subsequent processing. (A tabulation of representative references identifying many of these processes, and many catalysts having conceivably useful activity for these processes, is appended.)

It is an object of the present invention to provide a process for preparing a stream from which benzene-toluene-xylenes may be recovered, by catalytically treating by-product effluent streams from pyrolytic hydrocarbon cracking processes. A further object is to provide a process for treating such by-product effluent stream in a simplified, low severity, operation so as both to produce benzene-toluene-xylenes (BTX), and, simultaneously, to decrease the content of interfering components. Still another object is to remove those monoole-

fins and diolefins which have heretofore interfered with the solvent extraction of BTX from dripolene and the like.

SUMMARY OF THE INVENTION

5 Briefly, in accordance with the invention, a stream from which benzene, toluene, and xylenes may be recovered readily is prepared by contacting a pyrolitic hydrocarbon cracking by-product effluent stream, containing substantial amounts of interfering monolefins and diolefins, calcined with
10 a TEA-silicate molecular sieve catalyst under low severity hydrocarbon processing conditions. As a result of this treatment, not only are the olefins hydrogenated to non-interfering aliphatics, but a substantial fraction of the aliphatics is dehydrocyclized to benzene-toluene-xylenes.

15 One of the remarkable aspects of the invention is that the same low severity conditions of temperature, pressure, and space velocity, which are suitable for hydrogenation with a TEA-silicate catalyst, are also suitable for the dehydrogenation reaction involved in aromatization. Thus, a simple processing scheme, with only a single reactor stage, is often adequate both to reduce to a minimal content, or eliminate the olefinic constituents that would interfere with the economic recovery of aromatics, and to produce benzene-toluene-xylenes from the feed stream.

25 A further important advantage of the invention resides in its ability to process any of a variety of the by-product effluent streams from pyrolitic cracking processes. As set out more fully below, these by-product effluent streams customarily include a C_4 fraction composed predominantly of
30 butanes, butenes, and butadiene; a C_5 fraction composed mainly of pentanes, pentenes, pentadienes and cyclic C_5 compounds; a C_6 - C_8 "dripolene" fraction containing BTX aromatics together with interfering olefins (i.e., having a similar boiling range);

and a C₉-plus fraction, including some BTX along with higher alkylated benzenes and polynuclear aromatics and aliphatics. Each of these streams, plus others that may be present in a particular plant may be processed according to the invention.

5 The calcined TEA-silicate catalyst for use with the present invention, to be identified more fully below, is described in Grose et al. U.S. 4,104,294. It is believed to be isostructural with zeolite ZSM-12; see Rosinski et al. U.S. 3,832,449. TEA-silicates are crystalline metal organosilicates
10 having identifiable X-ray diffraction characteristics and other properties that have been described in the reference above.

Various other aspects of the invention are set out below.

15 DESCRIPTION OF PREFERRED EMBODIMENTS

1. Pyrolytic Cracking Processes

Pyrolytic cracking processes for the preparation of light olefins and diolefins such as ethylene, propylene, and/or butadiene, have been described in the literature, and
20 accordingly no detailed exposition is called for here.

In essence, the thermal pyrolysis, or cracking, of petroleum fractions may utilize as feed stocks hydrocarbons such as ethane, LPG (liquefied petroleum gas, chiefly propane with a few percent butanes), naphtha, heavy gas oil, or crude
25 petroleum oil. These are subjected to controlled high temperature, low pressure, short time, pyrolytic cracking to produce the desired product or products. Thereafter the reactor effluent is subjected to a combination of condensation, fractional distillation, absorption, and perhaps other unit
30 operations, to segregate various effluent streams enriched in one or more desirable components. The precise arrangement of product recovery streams forms no part of the present invention,

and indeed it is probable that no two pyrolytic cracking plants utilize the same recovery scheme.

For example, the reactor effluent liquid may be subjected to fractional distillation to separate one or more fractions rich in benzene (B.P. 80.103°C.), toluene (B.P. 110.623°C.), and/or the xylenes, namely ethylbenzene (B.P. 136.187°C.), p-xylene (B.P. 138.348°C.), m-xylene (B.P. 139.102°C.), and o-xylene (B.P. 144.414°C.). This fraction, or fractions is desirably solvent extracted, as for example by the Udex or Solfolane process, to recover the BTX aromatic/aromatics.

In the absence of prior treatment, such as by the process of the present invention, solvent extraction is ineffective to extract the aromatics from the remaining aliphatics, inasmuch as solvents selective for aromatics will also extract many olefins and diolefins. However, the diolefins and the aromatics cannot be separated by fractional distillation; for example, benzene, with a boiling point of 80.103°C., is not easily distilled from the 2,4-hexadienes, which boil at about 80.0°C. Similarly, the various dimethylpentenes boil within a range of 72.2°C. to 85.0°C.

Be that as it may, and howsoever produced or constituted, there inevitably will be one or more by-product effluent streams which contain diverse mixtures of hydrocarbon (and perhaps non-hydrocarbon) components, varying both with respect to boiling point and chemical classification. It is this diversity that either complicates or prevents the recovery of useable components.

By way of example, in an illustrative pyrolytic cracking plant, the total reactor effluent may be segregated into a predominantly gaseous fraction including recoverable ethylene and propylene; a crude C₄ fraction, a distillation

cut which includes hydrocarbons with primarily four carbon atoms each; a crude C_5 fraction, another distillation cut which primarily contains hydrocarbon molecules with five carbon atoms each, and generally containing a large quantity of unsaturated and cyclic compounds, including olefins and lesser amounts of C_4 's and lighter C_6 's and heavier; a C_6-C_8 fraction, sometimes referred to as pyrolysis gasoline or dripolene; and a C_9 plus fraction, a heavier distillation cut which primarily includes hydrocarbons with at least nine carbon atoms, along with lesser amounts of C_5-C_8 hydrocarbons. The C_9 fraction generally is produced as the distillation bottoms from the processing of dripolene to remove pyrolysis gasoline, and contains components as widely varying as styrene, ethyltoluenes, and trimethylbenzenes, to heavier compounds including ethylnaphthalene, diphenyl, and dimethylnaphthalene.

An illustrative C_4 fraction, giving both the range and a typical composition, is set out in Table I below:

TABLE I

Illustrative C₄'s Composition

5	<u>Compound</u>	<u>Observed Range</u>	<u>Typical Composition</u>
	Lights	0.4-5.0 wt. %	1.1
	Methylacetylene, Propadiene	0.1-1.0	0.7
	n & i-Butane	2.4-15.0	3.8
10	1-Butene and Isobutylene	20.0-39.0	33.8
	t-2-Butene	4.0-7.0	5.7
	c-2-Butene	3.0-5.0	4.5
	1,3-Butadiene	41.0-54.0	44.6
	Vinylacetylene	0.4-1.5	0.7
15	Ethylacetylene	0.1-0.5	0.2
	C ₅ +	0.2-5.0	4.1

Illustrative C₅ compositions, from two different plants, "A" and "B," are likewise represented in Table II below:

20

TABLE II

Illustrative C₅'s Compositions

		<u>Plant A</u>		<u>Plant B</u>	
		<u>Observed Range</u>	<u>Typical Composition</u>	<u>Observed Range</u>	<u>Typical Composition</u>
25	C ₄ and Lighter	0-1.5 wt. %	0.7	1.4-8.1	5.5
	n & i-Pentanes	0.14.4	7.2	17.3-44.60	23.6
	C ₅ Olefins	0.1-11.3	4.6	6.6-37.4	9.9
	Pentadienes	9.7-35.3	20.0	3.5-12.9	4.2
	Isoprene	2.4-43.0	13.1	5.0-16.8	5.9
30	Cyclopentane	1.6-7.5	3.2	0-2.0	---
	Cyclopentene	2.2-10.3	5.4	2.0-14.4	2.3
	Cyclopentadiene	0.60-2.8	1.4	1.0-20.6	4.6
	C ₆ Paraffins	1.1-7.2	4.2	1.3-10.5	10.1

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TABLE II (Cont.)

		<u>Plant A</u>		<u>Plant B</u>	
		<u>Observed Range</u>	<u>Typical Composition</u>	<u>Observed Range</u>	<u>Typical Composition</u>
5	C ₆ Olefins	---	---	0.3.0	0.2
	Benzene	0.4-5.1	1.3	0-23.8	23.8
	Dicyclopentadiene	19.3-48.1	32.1	1.0-21.0	1.8
	Other C ₆₊	1.5-14.8	6.8	0.9.0	8.1

Illustrative C₉ compositions, again from Plant "A" and Plant "B",

10 are described in Table III below:

TABLE III

Illustrative C₉'s Compositions

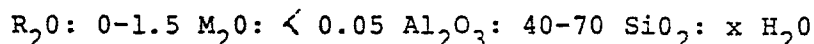
		<u>Plant A</u>		<u>Plant B</u>	
		<u>Observed Range</u>	<u>Typical Composition</u>	<u>Observed Range</u>	<u>Typical Composition</u>
15	C ₅ -C ₈				
	Nonaromatics	0.5-5.4	0.5	0.2-3.4	0.2
	BTX	0-9.8	1.7	0-31.9	1.2
20	Styrene	0.3-10.0	1.8	0.16.8	5.0
	Dicyclopentadiene	7.2-40.0	29.2	4.7-42.0	40.5
	Methyl dicyclopentadiene and Dimethyldi- cyclopentadiene	4.4-21.2	4.4	0-6.5	1.6
25	Methyl Styrenes	2.3-19.0	6.8	0.15.0	3.6
	C ₃ Benzenes	8.0-26.0	12.7	0-12.5	7.3
	Indane	0.2-16.9	13.8	0-6.9	0.2
	Indene	3.9-15.6	9.9	1.0-13.0	9.8
30	Naphthalenes	0.6-9.3	3.5	3.0-15.0	14.1
	Other C ₁₀₊	10.7-32.6	15.7	14.6-48.6	16.7

It will be appreciated, as noted earlier, that these compositions may vary quite widely, depending upon the initial feed to the pyrolitic cracking unit, the type of pyrolitic cracking unit, conditions, in the pyrolitic unit, and the type and conditions of the product recovery section. The by-product effluent streams may likewise be blended with each other where this is desired, or may include recycle components from elsewhere in the product recovery section.

2. Catalyst

The catalyst used in the present process is commonly termed calcined TEA-silicate, a newly discovered crystalline silica polymorph described in Grose et al. U.S. 4,104,294.

The class of crystalline metal organosilicates are synthesized from reaction systems essentially free of aluminum-containing reagents and are either entirely free of framework AlO_4 -tetrahedra or contain no crystallographically significant amounts thereof. These compositions, as a class, are called TEA-silicates and have the following as-synthesized composition in terms of moles of oxides:



wherein R represents the tetraethylammonium cation, M represents an alkali metal cation, and x has a value of from 0 to 15 depending upon the degree of hydration of the composition. TEA-silicates possess a definite crystal structure whose X-ray powder diffraction pattern shows the following significant lines:

TABLE IV

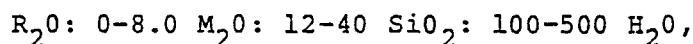
<u>Interplanar Spacing d-(A)</u>	<u>Relative Intensity</u>
11.9 ± 0.2	S
10.2 ± 0.2	M
4.76 ± 0.1	W
4.29 ± 0.08	VS
3.87 ± 0.07	VS

TABLE IV--(Cont.)

	<u>Interplanar Spacing d-(A)</u>	<u>Relative Intensity</u>
	3.66 \pm 0.07	W
	3.49 \pm 0.07	W
	3.38 \pm 0.07	M
	3.20 \pm 0.06	W
5	3.05 \pm 0.05	W
	2.64 \pm 0.03	W

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation-counter spectrometer with a strip-chart pen recorder was used. The peak heights "I" and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities 100 I/I₀, where I₀ is the intensity of the strongest line or peak and d (obs.), the interplanar spacing in A corresponding to the recorded lines, were calculated. In Table IV the relative intensities are given in terms of the symbols S=strong, M=medium, W=weak and VS=very strong. It should be understood that this X-ray diffraction pattern is characteristic of all the forms of TEA-silicate.

The crystalline metal organosilicates can be suitably synthesized by preparing a reaction system which in terms of moles of oxides has a composition within the range:



wherein R represents the tetraethylammonium cation and M represents an alkali metal cation, preferably sodium, potassium or lithium, said reaction mixture having a pH of greater than 12. The reaction mixture is preferably formed from the hydroxide of the alkali metal employed and the tetraethylammonium cation can be provided from an appropriate salt or base thereof such as tetraethylammonium bromide and tetraethylammonium hydroxide. Any reactive source of SiO₂ such as silica sols, gels, solid amorphous silicas or alkali metal silicates can be utilized in the same manner as SiO₂ is con-

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ventionally supplied to reaction mixtures in the preparation of synthetic zeolites. The reaction system is maintained at a temperature within the range of 125° to 150°C. until crystals of TEA-silicate are formed, usually a period of from about 70 to 250 hours. Thereafter the crystals are separated from the mother liquor and recovered by filtration or other conventional means. After washing with water, the TEA-silicate crystals are dried either in vacuum or an inert atmosphere such as air at moderate temperatures, about 100°-110°C.

The crystalline organosilicates described herein are substantially free of alumina, but may contain very minor amounts thereof due to the presence of alumina as an impurity in the reactants employed, principally the silica source. Accordingly, the molar ratio of alumina to silica will be in the range of zero to less than 0.005.

Neither the tetraethylammonium nor the alkali metal cations of the TEA-silicates can be removed by ion-exchange techniques. The organic cations, however, can be decomposed thermally by calcination at temperatures of 400°C. or higher in an oxidizing or inert atmosphere such as air or nitrogen, respectively. Thermal decomposition of the organic cations does not affect the essential crystalline structure of the composition and the X-ray powder diffraction pattern is essentially unaltered.

Calcination to thermally decompose the TEA cations produces an apparent pore diameter of greater than 6.2 Angstroms. Thereafter, the calcined TEA-silicate is desirably washed to remove any metals or trace contaminants.

When used in the present process, calcined TEA-silicate may be employed either alone or in intimate admixture with independently active catalytic components, as for example the noble metals such as platinum, or other catalytically active

metals such as molybdenum, vanadium, zinc, etc. The techniques of introducing catalytically active metals to a molecular sieve zeolite are disclosed in the literature, and preexisting metal incorporation techniques are suitable. See, for example, Rabo
5 et al. U.S. 3,236,761 and U.S. 3,236,762.

The physical form of the calcined TEA-silicate catalyst depends on the type of catalytic reactor being employed. Calcined TEA-silicate by itself is a fine-grain granule or powder, and is desirably compacted into a more
10 readily usable form (e.g., larger agglomerates), usually with a silica or alumina binder for fluidized bed reaction, or pills, prills, spheres, extrudates, or other shapes of controlled size to accord adequate catalyst-reactant contact. As indicated, the catalyst may be employed either as a fluidized catalyst, or in
15 a fixed or moving bed, and in one or more reaction stages.

3. Conversion Parameters

An unusual, if not unique, feature of the present invention is that the reaction conditions are low severity as compared with many preexisting processes. Indeed, the conver-
20 sion parameters, while broad, may be selected to provide a high degree of versatility, depending upon the feed composition and on the desired product quality.

With respect to temperature, a temperature within the range of about 300-700°C., more preferably within the range of
25 about 350-600°C., is adequate for many, if not all, conversions. Higher temperatures give more rapid and more complete reaction, but tend to produce undesirable by-products, chiefly coke, and may otherwise disturb the optimum balance of product composition with on-stream ease of operation.

30 The pressure, almost uniquely, is desirably quite low. Atmospheric pressure operation has been used successfully

in the laboratory, but under specific conditions may be as high as 100 atmospheres or more. A desirable range is from atmospheric pressure to about 7 atmospheres. High pressures facilitate hydrogenation; lower pressures facilitate dehydrocyclization. The optimum pressure will therefore depend on process economics, considering whether it is more desirable to hydrogenate olefins than to produce a high yield of BTX aromatics.

Process stream flow rate, as expressed in units of weight hourly space velocity (WHSV), or weight of hydrocarbon feed per unit weight of catalyst, is suitably within the range of about 0.1 to about 20, more desirably about 0.5-5.0. High WHSV's permit more economic plant construction, while lower WHSV's permit more complete reaction at given temperature-pressure conditions.

If desired, a gaseous or gasifiable diluent may be introduced along with the hydrocarbon feed to the silicalite catalyst. This diluent may be inert, typified by steam, nitrogen or a low boiling paraffin, or may be reactive with the feed under catalysis conditions (e.g., hydrogen). Hydrogen is particularly desirable as it minimizes coke formation and deposition on the catalyst, with resulting premature deactivation, and also facilitates hydrogenation. As demonstrated below, however, the technique of the present invention need not utilize hydrogen.

If either an inert or a reactive gas is employed, diluent/hydrocarbon molar (gas volume) ratios, optimally, of from 0.1 to about 10 may be employed.

It is usually necessary that the catalyst be regenerated, either periodically or continuously, to remove the carbonaceous coke-like deposits from the catalyst. In a fluidized bed operation, a portion of the catalyst is continuously withdrawn from the reactor and then subjected to regen-

eration by combustion with air or other oxygen containing gas, after which it is continuously recycled to the reactor. In a moving bed operation, the removal of catalyst followed by regeneration may be effected either continuously or periodically.

- 5 In a fixed bed operation, it is generally desirable that two or more reactors be used in parallel, so that when one is processing the hydrocarbon feed, the other is out of service and being regenerated. Regeneration conditions of approximately 450-650°C, preferably 500-600°C. may be employed.

10 4. Example I

A specific example for the conversion of a C₉-plus feed is presented below. From the data, it is apparent that olefins and diolefins are converted by hydrogenation; that acyclic and cyclic nonaromatic components are dehydrocyclized
15 to aromatic compounds; that C₉ plus alkylbenzenes, indane, indene, and methylstyrenes are converted in substantial part to the more desirable C₆-C₈ aromatics; and that, apparently, higher alkyl naphthalenes are converted by hydrogenolysis to recoverable naphthalene and methyl naphthalenes. Additionally, it is likely that
20 the organic sulfur and nitrogen contents are lowered.

In the example herein, a C₉ plus by-product hydrocarbon effluent from the thermal pyrolysis unit was reacted over 37g of 1/16 inch extrudates of TEA-silicate with a 15% alumina binder. The reaction vessel was a 3/4 inch OD stain-
25 less steel tubular reactor.

The reaction pressure was ambient; the reaction temperature was approximately 450°C.; and the space velocity of the feed varied from 0.7-0.8 g feed/g catalyst/hr. The molar ratio of SiO₂-to-Al₂O₃ in the catalyst was 377:1.

30 Samples of the liquid products, trapped in an ice water condenser, were taken after one hour and after six hours on stream. Five gas product samples were taken periodically.

The feed had the following analysis:

Analysis of C₉-Plus Hydrocarbon Feed

	<u>Compounds</u>	<u>Weight Percent</u>
5	C ₅ -C ₈ Nonaromatics	0.19
	Benzene	0.31
	Toluene	0.10
	Ethylbenzene, Mixed Xylenes	0.80
	Dicyclopentadiene, Styrene	45.46
10	C ₉ Alkylbenzenes, Methylstyrenes	10.61
	Indan	0.21
	Indene	9.83
	Naphthalene	12.67
	Methylnaphthalenes	1.45
15	Other C ₉ + Hydrocarbons	18.37

The gas samples were analyzed on a Hewlett Packard 5830A gas chromatograph equipped with a thermal conductivity detector. A forty foot stainless steel column with an OD of 1/8 inch packed with 20% tributylphosphate on 35/80 mesh

20 Chromasorb P (acid washed) was used. The thermal conductivity detector temperature was set at 250°C., and the column temperature was ambient (approximately 20-22°C.). Gas samples were injected into the column off-line, through an eight port gas switching valve, via a gas syringe. The sample gas volume
25 was approximately 0.3cc; the carrier gas rate was 30cc/min of helium.

Liquid samples for both product and feed were analyzed on a Hewlett Packard 5730A gas chromatograph, using a 5705A thermal conductivity detector. A ten foot stainless
30 steel column with an OD of 1/8 inch, packed with 15% Carbowax 20M on 40/60 mesh Chromasorb P (acid washed), was used. The

detector temperature was set at 250°C. The column was maintained in an oven, with a temperature programmed from 55°C. to 190°C. at 4°C./min; the injector temperature was 250°C. A sample size of approximately 2 ml. was used, and the helium carrier gas rate was 30cc/min.

The following yields were determined:

Product Analyses From Conversion
of C₉₊ Hydrocarbons Using TEA-Silicate

	<u>Compounds</u>	<u>Product</u>	<u>Composition</u>
		<u>(Weight Percent Yield)</u>	
		<u>1 hr.</u>	<u>6 hr.</u>
	Methane	8.8	0.3
	Ethane, Ethylene	1.3	0.3
	Propane	9.4	0.1
	Propylene	0.0	0.1
15	C ₄ 's	9.9	0.7
	C ₅ to C ₈ Nonaromatics	3.5	12.0
	Benzene	13.4	3.1
	Toluene	12.3	4.0
	Mixed Xylenes	10.1	6.7
20	C ₉₊ Hydrocarbons	31.3	72.8

Example II

A crude butadiene by-product hydrocarbon from an olefins production unit was reacted over 0.25 g of powdered catalyst (TEA-silicate) in a thermal chromatograph microreactor at 450°C. Crude butadiene flow rate was 5 cc/min at ambient pressure. The molar ratio of SiO₂-to-Al₂O₃ in the catalyst was 377:1. The reaction products were collected in a liquid nitrogen trap and then were allowed to purge into a gas chromatograph OV-101 column with a helium carrier gas. Analyses were run on both a flame detector and a thermal conductivity detector.

Example III

The extrudate catalyst used in Example I was tested in the microreactor for the conversion of crude butadiene by-product. All conditions and the amount of catalyst were the same as in Example II.

Analyses of the crude butadiene feed in Examples II and III, and of the products from the reactions are shown below:

Analysis of Crude Butadiene Feed

	<u>Compounds</u>	<u>Weight Percent</u>
10	C ₃ 's and lighter	1.24
	Isobutane	2.57
	n-Butane	8.68
	1-Butene, Isobutylene	33.74
	t-2-Butene	4.15
15	c-2-Butene	2.44
	1,3-Butadiene	45.72
	C ₄ Acetylenes	1.28
	C ₅ Hydrocarbons	0.19

20 Product Analyses From Conversion of Crude Butadiene Using TEA-Silicate Catalyst

	<u>Compounds</u>	<u>Example II</u>	<u>Example III</u>
	C ₁ -C ₄	32.5	38.2
	C ₅ +C ₆ Aliphatics	9.5	8.1
25	Benzene	3.9	3.3
	C ₇ Aliphatics	3.8	4.7
	Toluene	11.4	7.6
	C ₈ Aliphatics	3.1	6.3
	Ethylbenzene, Xylenes	14.3	11.3
30	C ₉ + Hydrocarbons	21.5	20.7

Thus it is apparent that there has been provided, according to the invention, a process that is uniquely effective in treating by-product effluent streams from pyrolytic cracking processes.

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References

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C L A I M S:

1. A low severity process for the preparation of a benzene-toluene-xylenes enriched stream containing minimal monoolefin and diolefin content, from a feed stream comprising a by-product effluent of a process for the pyrolytic cracking of hydrocarbons to produce light olefins or diolefins, said by-product effluent stream containing olefins and diolefins, said process comprising contacting said by-product effluent stream, under low severity conditions including a temperature within the range of about 300-700°C., a pressure within the range of about 0 to 100 atmospheres, and a weight hourly space velocity within the range of about 0.1 to about 20, with a catalyst essentially comprising a calcined TEA-silicate.
2. Process of claim 1 wherein said conditions include a temperature within the range of about 350-600°C., a pressure within the range of about 1-7 atmospheres, and a weight hourly space velocity within the range of about 0.5-5.0.
3. Process of claim 1 wherein said by-product effluent comprises a C₄ stream.
4. Process of claim 1 wherein said by-product effluent comprises a C₅ stream.
5. Process of claim 1 wherein said by-product effluent comprises a whole or fractionated dripolene stream.
6. Process of claim 1 wherein said feed stream is admixed with a diluent.
7. Process of claim 6 wherein said diluent is steam.
8. Process of claim 6 wherein said diluent is hydrogen.
9. Process of claim 6 wherein said diluent is a low boiling paraffin.
10. Process of claim 6 wherein said diluent is a mixture of a low boiling paraffin, hydrogen and/or steam.



EP 83200611.8

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D, X	<u>US - A - 4 104 294 (GROSE et al.)</u> * Claims; column 2, lines 65-68 * --	1	C 10 G 35/06 C 10 G 45/68
P, A	<u>US - A - 4 341 622 (TABAK et al.)</u> * Claims; column 1, line 26 - column 5, line 55 * --	1, 2, 8	
A	<u>US - A - 4 235 701 (KOPF)</u> * Claims; column 2, line 30 - column 3, line 54 * --	1, 2, 5, 8	
A	<u>EP - A1 - 0 023 802 (MOBIL OIL CORPORATION)</u> * Claims; page 2 - page 9, line 3 * -----	1, 2, 8	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 10 G 35/00 C 10 G 45/00 C 10 G 47/00 C 10 G 49/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 01-08-1983	Examiner STÖCKLMAYER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	