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(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).

(72) Inventors: CHENG, Jane, Chi-Ya; 26 Deer Trail Drive, Clarksburg, NJ 08510 (US). SMITH, Charles, Morris; 19 Locust Lane, Princeton, NJ 08540 (US). WALSH, Dennis, Edward; 36 Redwood Drive, Richboro, PA 18954 (US).

(74) Agents: SUNG, Tak, K. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).

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(54) Title: LIQUID PHASE ETHYLBENZENE SYNTHESIS

(57) Abstract

A process for the production of ethylbenzene comprises alkylating benzene with ethylene in the liquid phase at a temperature of 150 to 315 °C in the presence of a catalyst comprising calcined aluminosilicate MCM-49.

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LIQUID PHASE ETHYLBENZENE SYNTHESIS

This invention relates to a process for the liquid phase synthesis of ethylbenzene.

Ethylbenzene is a valuable commodity chemical which is currently used on a large scale industrially for the production of styrene monomer. Ethylbenzene may be produced by a number of different chemical processes but one process which has achieved a significant degree of commercial success is the vapor phase alkylation of benzene with ethylene in the presence of a solid, acidic ZSM-5 zeolite catalyst. In the production of ethylbenzene by this process, ethylene is used as the alkylating agent and is reacted with benzene in the presence of the catalyst at temperatures which vary between the critical temperature of benzene up to 900°F (about 480°C) at the reactor inlet. The reactor bed temperature may be as much as 150°F (about 85°C) above the reactor inlet temperature and typical temperatures for the benzene/ethylene reaction vary from 600° to 900°F (315° to 480°C), but are usually maintained above about 700°F.(about 370°C.) in order to keep the content of the more highly alkylated benzenes such as diethylbenzene at an acceptably low level. Pressures typically vary from atmospheric to 3000 psig (100 to 20785 kPa) with a molar ratio of benzene to ethylene from 1:1 to 25:1, usually about 5:1 (benzene:ethylene). Space velocity in the reaction is high, usually in the range of 1 to 6, typically 2 to 5, WHSV based on the ethylene flow, with the benzene space velocity varying accordingly, in proportion to the ratio of the reactants. The products of the reaction include ethylbenzene which is obtained in increasing proportions as temperature increases together with various polyethylbenzenes, principally diethylbenzene (DIEB) which also are produced in increasing amounts as reaction temperature increases. Under favorable operating conditions on the industrial scale, an ethylene conversion in excess of 99.8 weight percent may be obtained at the start of the cycle.

In the commercial operation of this process, the polyalkylated benzenes, including both polymethylated and polyethylated benzenes are recycled to the alkylation reactor in which the reaction between the benzene and the ethylene takes place. By recycling the by-products to the alkylation reaction, increased conversion is obtained as the polyethylated benzenes (PEB) are converted to ethylbenzene (EB). In addition, the presence of the PEB during the alkylation reaction reduces formation of these species through equilibration of the components because at a given feed composition and under specific operating conditions, the PEB recycle will reach equilibrium at a certain level. This commercial process is known as the Mobil/Badger process and is described in more detail in an article by Francis G. Dwyer, entitled "Mobil/Badger Ethylbenzene Process-Chemistry and Catalytic Implications", appearing on pages 39-50 of a book entitled Catalysis of Organic Reactions, edited by William R. Moser, Marcel Dekker, Inc., 1981.

Ethylbenzene production processes are described in U.S. Patents Nos. 3,751,504 (Keown), 4,547,605 (Kresge), and 4,016,218 (Haag). The process described in U.S. 3,751,504 is of particular note since it includes a separate transalkylation step in the recycle loop which is effective for converting a significant proportion of the more highly alkylated products to the desired ethylbenzene product. Other processes for the production of ethylbenzene are disclosed in U. S. Patents Nos. 4,169,11 (Wight) and 4,459,426 (Inwood), in both of which a preference for large pore size zeolites such as zeolite Y is expressed, in distinction to the intermediate pore size zeolites used in the processes described in the Keown, Kresge and Haag patents. U.S. Patent No. 3,755,483 (Burress) describes a process for the production of ethylbenzene using zeolite ZSM-12 as the alkylation catalyst.

Ethylbenzene (EB) can be synthesized from benzene and ethylene (C_2=) over a variety of zeolitic catalysts in either the liquid phase or in the vapor phase. An advantage of a liquid phase process is its low operating temperature and the resulting low content of by-products.

U.S. Patent No. 4,891,458 describes the liquid phase synthesis of ethylbenzene with zeolite beta.

U.S. Patent No. 5,149,894 describes the liquid phase synthesis of ethylbenzene with a crystalline aluminosilicate material designated SSZ-25.

According to the invention, there is provided a process for the production of ethylbenzene comprising alkylating benzene with ethylene in the liquid phase at a temperature of 150 to 315°C in the presence of a catalyst comprising the calcined aluminosilicate zeolite MCM-49 having, in its as-synthesized form, the X-ray diffraction pattern of Table 1, and, in its calcined form, the X-ray diffraction pattern of Table 2.

The catalyst used in the present liquid phase alkylation reaction comprises a crystalline material designated MCM-49. MCM-49 and methods for its preparation are described in U.S. Patent No. 5,236,575.

MCM-49 may exist in a number of forms depending, for example, upon its composition and thermal history. A particular form of MCM-49, based upon composition, is the aluminosilicate form, wherein the framework of the MCM-49 crystal structure consists essentially of silica and alumina. Forms of MCM-49, based upon thermal history, include the as-synthesized form and the calcined form. These as-synthesized and calcined forms of MCM-49 are described more particularly hereinafter.

MCM-49 has been discovered to be active and very selective for liquid phase ethylbenzene synthesis. This selectivity advantage can be translated to a lower benzene recycle ratio and lower down stream separation costs while maintaining product quality.

In the as-synthesized form, MCM-49 appears to be a single crystalline phase. It can be prepared in essentially pure form with little or no detectable impurity crystal phases and has an X-ray diffraction pattern which is distinguished from the patterns of other known as-synthesized or thermally treated crystalline materials by the lines listed in Table 1 below:

TABLE 1

Interplanar d-Spacing (A)	Relative Intensity, I/Io x 100
13.15 ± 0.26	w-s*
12.49 ± 0.24	vw
11.19 ± 0.22	m-s
6.43 ± 0.12	w
4.98 ± 0.10	w
4.69 ± 0.09	w
3.44 ± 0.07	vs
3.24 ± 0.06	w

* shoulder

In its calcined form, MCM-49 transforms to a single crystal phase with little or no detectable impurity crystal phases having an X-ray diffraction pattern which is not readily distinguished from that of MCM-22, but distinguishable from the patterns of other known crystalline materials. The X-ray diffraction pattern of the calcined form of MCM-49 includes the lines listed in Table 2 below:

TABLE 2

Interplanar d-Spacing (A)	Relative Intensity, I/Io x 100
12.41 ± 0.24	vs
11.10 ± 0.22	s
8.89 ± 0.17	m-s
6.89 ± 0.13	w
6.19 ± 0.12	m
6.01 ± 0.12	w
5.56 ± 0.11	w
4.96 ± 0.10	w
4.67 ± 0.09	w
4.59 ± 0.09	w
4.39 ± 0.09	w
4.12 ± 0.08	w
4.07 ± 0.08	w-m
3.92 ± 0.08	w-m
3.75 ± 0.07	w-m
3.57 ± 0.07	w
3.43 ± 0.07	s-vs
3.31 ± 0.06	w
3.21 ± 0.06	w
3.12 ± 0.06	w
3.07 ± 0.06	w
2.83 ± 0.05	w
2.78 ± 0.05	w
2.69 ± 0.05	w
2.47 ± 0.05	w
2.42 ± 0.05	w
2.38 ± 0.05	w

MCM-49, in its calcined form, may have a bulk silica:alumina (SiO_2:Al_2O_3) molar ratio of less than about 24:1, preferably less than about 20:1.

MCM-49 can be prepared from a reaction mixture containing sources of alkali or alkaline earth metal (M), e.g., sodium or potassium, cation, an oxide of trivalent element X, e.g., aluminum, an oxide of tetravalent element Y, e.g., silicon, directing agent (R), and water, said reaction mixture having a composition, in terms of mole ratios of oxides, within the following ranges:

Reactants	Useful	Preferred
YO_2/X_2O_3	12 to <35	18 to 31
H_2O/YO_2	10 to 70	15 to 40
OH^-/YO_2	0.05 to 0.50	0.05 to 0.30
M/YO_2	0.05 to 3.0	0.05 to 1.0
R/YO_2	0.2 to 1.0	0.3 to 0.5

In this synthesis method, if more than one X component is present, at least one should be present such that the YO_2/x_2O_3 molar ratio thereof is less than about 35. For example, if aluminum oxide and gallium oxide components are used in the reaction mixture, at least one of the YO_2/Al_2O_3 and YO_2/Ga_2O_3 molar ratios should be less than about 35. If only aluminum is present, the YO_2/Al_2O_3 ratio should be less than about 35.

The source of YO_2 may be soluble or insoluble, but is preferably comprised predominately of solid YO_2, for example at least about 30 wt.% solid YO_2 in order to obtain the crystal product of the invention. Where YO_2 is silica, the use of a silica source containing at least about 30 wt.% solid silica, e.g., Ultrasil (a precipitated, spray dried silica containing about 90 wt.% silica) or HiSil (a precipitated hydrated SiO_2 containing about 87 wt.% silica, about 6 wt.% free H_2O and about 4.5 wt.% bound and H_2O of hydration and having a particle size of about 0.02 micron) favors crystalline MCM-49 formation from the above mixture. Preferably, therefore, the solid YO_2, e.g., silica, source contains at least about 30 wt.% solid YO_2, e.g., silica, and more preferably at least about 40 wt.% solid YO_2, e.g., silica.

Crystallization of MCM-49 can be carried out under either static or stirred conditions in a suitable reactor vessel, such as for example, polypropylene jars or teflon lined or stainless steel autoclaves, at a temperature of 80 to 225°C for a time of 24 hours to 60 days. Thereafter, the crystals are separated from the liquid and recovered.

Synthesis of MCM-49 may be facilitated by the presence of at least 0.01 percent, preferably 0.10 percent and still more preferably 1 percent, seed crystals (based on total weight) of crystalline product. Useful seed crystals include MCM-22 and/or MCM-49.

Directing agent R for making MCM-49 may be selected from the group consisting of cycloalkylamine, azacycloalkane, diazacycloalkane, and mixtures thereof, alkyl comprising from 5 to 8 carbon atoms. Non-limiting examples of R include cyclopentylamine, cyclohexylamine, cycloheptylamine, hexamethyleneimine, heptamethyleneimine, homopiperazine, and combinations thereof. The preferred directing agent is hexamethyleneimine.

The MCM-49 used in process of the invention may be composited with another material which is resistant to the temperatures and other conditions employed in the process. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays and/or oxides such as alumina, silica, silica-alumina, zirconia, titania, magnesia or mixtures of these and other oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Clays may also be included with the oxide type binders to modify the mechanical properties of the catalyst or to assist in its manufacture. Use of a material in conjunction with the MCM-49, i.e., combined therewith or present during its synthesis, which itself is catalytically active may change the conversion and/or selectivity of the catalyst. Inactive materials suitably serve as diluents to control the amount of conversion so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions and function as binders or matrices for the catalyst. The relative proportions of finely divided crystalline material and inorganic oxide matrix vary widely, with the MCM-49 content ranging from 1 to 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 weight percent of the composite.

The alkylation reaction is carried out in the liquid phase at a temperature of 150 to 315°C (300 to 600°F), preferably 150° to 260°C (300 and 500°F), and most preferably 205° to 260°C (400° to 500°F).

Pressures during the alkylation step may be as high as about 3000 psig, (about 20875 kPa), generally will not exceed 1000 psig (about 7000 kPa) and will be 400 to 800 psig (2860 to 5620 kPa). The reaction may be carried out in the absence of hydrogen and accordingly the prevailing pressures are those of the reactant species. The space velocity may be from 0.1 to 10, preferably 0.1 to 1 and most preferably 0.2 to 0.5, based on the ethylene feed. The ratio of the benzene to the ethylene in the alkylation reactor may be from 1:1 to 30:1 molar (benzene:ethylene, fresh feed), normally 5:1 to 20:1 and preferably 5:1 to 10:1 molar.

The alkylation process can be carried out as a batch-type, semi-continuous or continuous operation utilizing a fixed, fluidized or moving bed catalyst system.

The invention will now be more particularly described with reference to the Examples and the accompanying drawings, in which:

Figure 1 is a graph showing a comparison of the activities of MCM-49 and MCM-22 in the liquid phase synthesis of ethylbenzene.

Figure 2 is a graph showing a comparison of the selectivities of MCM-49 and MCM-22 in the liquid phase synthesis of ethylbenzene.

EXAMPLE 1

A 2.24 part quantity of 45% sodium aluminate was added to a solution containing 1.0 part of 50% NaOH solution and 43.0 parts H_2O in an autoclave. An 8.57 part quantity of Ultrasil precipitated silica was added with agitation, followed by 4.51 parts of hexamethyleneimine (HMI).

The reaction mixture had the following composition, in mole ratios:

SiO_2/Al_2O_3 = 23
OH^-/SiO_2 = 0.21
Na/SiO_2 = 0.21
HMI/SiO_2 = 0.35
H_2O/SiO_2 = 19.3

The mixture was crystallized at 150°C for 84 hours with stirring. The product was identified as MCM-49 and had the X-ray pattern which appears in Table 3.

The chemical composition of the product was, in wt.%:

N	1.70
Na	0.70
Al_2O_3	7.3
SiO_2	74.5
Ash	84.2

The silica/alumina mole ratio of the product was 17.3.

The sorption capacities, after calcining at 538°C for 9 hours were, in wt.%:

Cyclohexane, 40 Torr	10.0
n-Hexane, 40 Torr	13.1
H_2O, 12 Torr	15.4

A portion of the sample was calcined in air for 3 hours at 538°C. This material exhibited the X-ray diffraction pattern shown in Table 4.

TABLE 3

Degrees 2-Theta	Interplanar d-spacing (A)	I/Io
3.1	28.5	18
3.9	22.8	7+
6.81	12.99	61 sh
7.04	12.55	97
7.89	11.21	41
9.80	9.03	40
12.76	6.94	17
13.42	6.60	4*
13.92	6.36	17
14.22	6.23	11
14.63	6.05	2
15.81	5.61	15
17.71	5.01	4
18.86	4.71	4
19.23	4.62	6
20.09	4.42	27
20.93	4.24	8
21.44	4.14	17
21.74	4.09	37
22.16	4.01	17
22.56	3.94	58
23.53	3.78	26
24.83	3.59	22
25.08	3.55	10
25.86	3.45	100
26.80	3.33	28
27.53	3.24	21
28.33	3.15	15
28.98	3.08	4
29.47	3.03	2
31.46	2.843	4
32.08	2.790	6
33.19	2.699	9
34.05	2.633	5
34.77	2.580	4
36.21	2.481	2
36.90	2.436	3
37.68	2.387	8

sh = Shoulder
+ = Non-crystallographic MCM-49 peak
* = Impurity peak

TABLE 4

Degrees 2-Theta	Interplanar d-spacing (A)	I/Io
3.2	28.0	9+
3.9	22.8	7+
6.90	12.81	48 sh
7.13	12.39	100
7.98	11.08	46
9.95	8.89	53
12.87	6.88	10
14.32	6.18	36
14.74	6.01	11
15.94	5.56	17
17.87	4.96	2
19.00	4.67	5
19.35	4.59	3
20.24	4.39	14
21.06	4.22	5
21.56	4.12	15
21.87	4.06	25
22.32	3.98	12
22.69	3.92	41
23.69	3.76	23
24.95	3.57	19
25.22	3.53	4
25.99	3.43	90
26.94	3.31	20
27.73	3.22	17
28.55	3.13	11
29.11	3.07	3
29.63	3.01	2
31.59	2.833	6
32.23	2.777	4
33.34	2.687	9
34.35	2.611	4
34.92	2.570	3
36.35	2.471	2
37.07	2.425	2
37.82	2.379	6

sh = Shoulder
\+ = Non-crystallographic MCM-49 peak

EXAMPLE 2

The calcined portion of the product of Example 1 was ammonium exchanged and calcined at 538°C in air for 3 hours to provide the hydrogen form transformation product of the crystalline MCM-49. The Alpha Test proved this material to have an Alpha Value of 308.

EXAMPLE 3

Sodium aluminate comprising 40 wt.% Al_2O_3, 33 wt.% NaO_2, and 27 wt.% H_2O was added to a solution containing NaOH and H_2O in an autoclave. Ultrasil precipitated silica was then added with agitation, followed by aminocycloheptane (R) directing agent to form a reaction mixture.

The reaction mixture had the following composition, in mole ratios:

SiO_2/Al_2O_3 = 33.3
OH^-/SiO_2 = 0.18
Na/SiO_2 = 0.18
R/SiO_2 = 0.35
H_2O/SiO_2 = 18.8

The mixture was crystallized at 143°C for 192 hours with stirring. The product was identified as MCM-49 and had the X-ray pattern which appears in Table 5.

The chemical composition of the product was, in wt.%:

N	1.51
Na	0.83
Al_2O_3	4.6
SiO_2	74.2
Ash	79.2

The silica/alumina mole ratio of the product was 27.4.

The sorption capacities, after calcining at 538°C for 9 hours were, in wt.%:

Cyclohexane, 40 Torr	7.5
n-Hexane, 40 Torr	14.1
H_2O, 12 Torr	13.5

TABLE 5

Degrees 2-Theta	Interplanar d-spacing (A)	I/Io
4.1	21.4	1
6.87	12.87	41
7.14	12.38	100
7.98	11.09	26
9.88	8.95	18
12.85	6.89	14
14.00	6.33	10
14.31	6.19	11
14.74	6.01	2
15.88	5.58	13
17.79	4.99	4
18.95	4.68	6
19.34	4.59	7
20.20	4.40	18
21.06	4.22	7
21.51	4.13	12
21.82	4.07	27
22.63	3.93	46
23.60	3.77	19
24.90	3.58	25
25.14	3.54	7
25.92	3.44	90
26.82	3.32	26
27.66	3.22	13
28.43	3.14	12
29.03	3.08	4
29.45	3.03	3
31.51	2.839	4
32.15	2.784	5
33.24	2.695	8
34.13	2.627	4
34.84	2.575	2
36.26	2.477	3
36.97	2.431	3
37.73	2.384	7

EXAMPLE 4

In order to provide a catalyst for comparative testing, a catalyst comprising MCM-22 was prepared as described hereinafter.

1.71 parts of 45% sodium aluminate solution were added to a solution containing 1.0 parts of 50% NaOH solution and 43.0 parts of H_2O in an autoclave. 8.57 parts of Ultrasil precipitated silica was then added with agitation, followed by 4.51 parts of HMI.

The reaction mixture had the following composition, in mole ratios:

SiO_2/Al_2O_3 = 30
OH^-/SiO_2 = 0.18
R/SiO_2 = 0.35
H_2O/SiO_2 = 19.4

The mixture was crystallized at 149°C for 78 hours with stirring. The chemical composition of the product was, in wt.%:

N	1.80
Na	0.50
Al_2O_3	5.5
SiO_2	76.2
Ash	80.5
SiO_2/Al_2O_3, mole ratio	23.5/1

The sorption capacities, after calcining at 538°C for 6 hours were, in wt.%:

Cyclohexane, 40 Torr	12.6
n-Hexane, 40 Torr	9.3
H_2O, 12 Torr	15.3

A portion of the uncalcined MCM-22 precursor drycake was mixed with alumina (Davison VFA) in proportions to give 65% MCM-22/35% alumina on a 100% solids basis. Deionized (DI) water was added to give an extrudable mull and the mix extruded to 1/16 inch diameter and dried at 120°C. The dried extrudate was calcined in flowing nitrogen at 482°C for 3 hours. It was then charged to a column and exchanged 2 times for 1 hour with 1N NH_4NO_3 solution (5 ml solution per gram of extrudate) at room temperature, washed with DI water, and dried at 120°C. The extrudate was then calcined in flowing air at 538°C for 6 hours.

EXAMPLE 5

A catalyst comprising MCM-49 was prepared as described hereinafter.

A portion of the uncalcined MCM-49 precursor drycake as prepared in Example 1 was mixed with alumina (LaRoche Versal 250) in proportions to give 65% MCM-49/35% alumina on a 100% solids basis. DI water was added to give an extrudable mull and the mix extruded to 1/16 inch diameter and dried at 120°C. The dried extrudate was calcined in flowing nitrogen at 482°C for 6 hours. It was then charged to a column and exchanged 3 times for 1 hour with 1N NH_4NO_3 solution (5 ml solution per gram of extrudate) at room temperature, washed with DI water, and dried at 120°C. The extrudate was heated in flowing nitrogen to 482°C, the atmosphere switched to flowing air, the temperature raised to 538°C, and finally calcined in flowing air for 12 hours at 538°C.

EXAMPLE 6

The catalysts of Examples 4 and 5 were evaluated for the liquid phase alkylation of benzene with ethylene. More particularly, a three-zone isothermal fixed-bed unit was used to evaluate the catalysts comprising MCM-49 and MCM-22. Two grams of each catalyst (1/16" diameter x 1/16" length) were diluted to ~20 cc with 20-40 mesh vycor chips to make up the active bed. Benzene was fed as liquid while $C_2=$ was fed as gas to the top of the reactor. The reactor was operated at 3550 kPa (500 psig), 4.5-7.5 benzene/$C_2=$ molar ratio, 0.55-3.3 $C_2=$ WHSV, and 160-320°C. Off gases were analyzed on a Carle refinery gas analyzer and liquid products were analyzed on a Varian 3700 GC equipped with an SPB-5 capillary column. Ethylene conversion was determined by measuring unreacted $C_2=$ offgas relative to feed $C_2=$. Total material balances were 100 ± 2%.

The activity of the catalysts, measured at 220°C, 3550 kPa (500 psig), and 5.5 benzene/$C_2=$ molar ratio, are compared in Figure 1. At constant C_2= conversion, the C_2= WHSV with MCM-49 is slightly higher than that with MCM-22, i.e., MCM-49 is slightly more active than MCM-22.

The selectivity of the catalysts is compared in the following table.

Catalyst	MCM-22	MCM-49
Product dist. (mol%)		
EB	94.0	95.3
DEB	5.7	4.5
TEB	0.2	0.1
Σ	99.9	99.9
xylenes	0.00	0.00
n-C_3-Bz/cumene	0.00	0.00
sec-C_4-Bz	0.07	0.06
other C_9+ aromatics	0.02	0.02
Σ (by products)	0.09	0.08

The data show that although 99.9 mol% overall selectivity to ethylbenzene (EB), diethylbenzene (DEB), and triethylbenzene (TEB) was observed for both catalysts, MCM-49 is more selective for the desired EB product. It produced 20% less DEB+TEB than MCM-22. The higher selectivity of MCM-49, presented as DEB/EB molar ratio, at other temperatures is shown in Figure 2: in liquid phase (<260°C), MCM-49 is more selective (lower DEB/EB ratio) than MCM-22.

Claims:

1. A process for the production of ethylbenzene comprising alkylating benzene with ethylene in the liquid phase at a temperature of 150 to 315°C in the presence of an catalyst comprising calcined aluminosilicate MCM-49, said MCM-49 having, in its as-synthesized form, the X-ray diffraction pattern of Table 1, and having, in its calcined form, the X-ray diffraction pattern of Table 2.

2. A process according to claim 1, wherein said MCM-49 in said catalyst has a bulk silica:alumina molar ratio of less than 24:1.

3. A process according to claim 1, wherein said MCM-49 in said catalyst has a bulk silica:alumina molar ratio of less than 20:1.

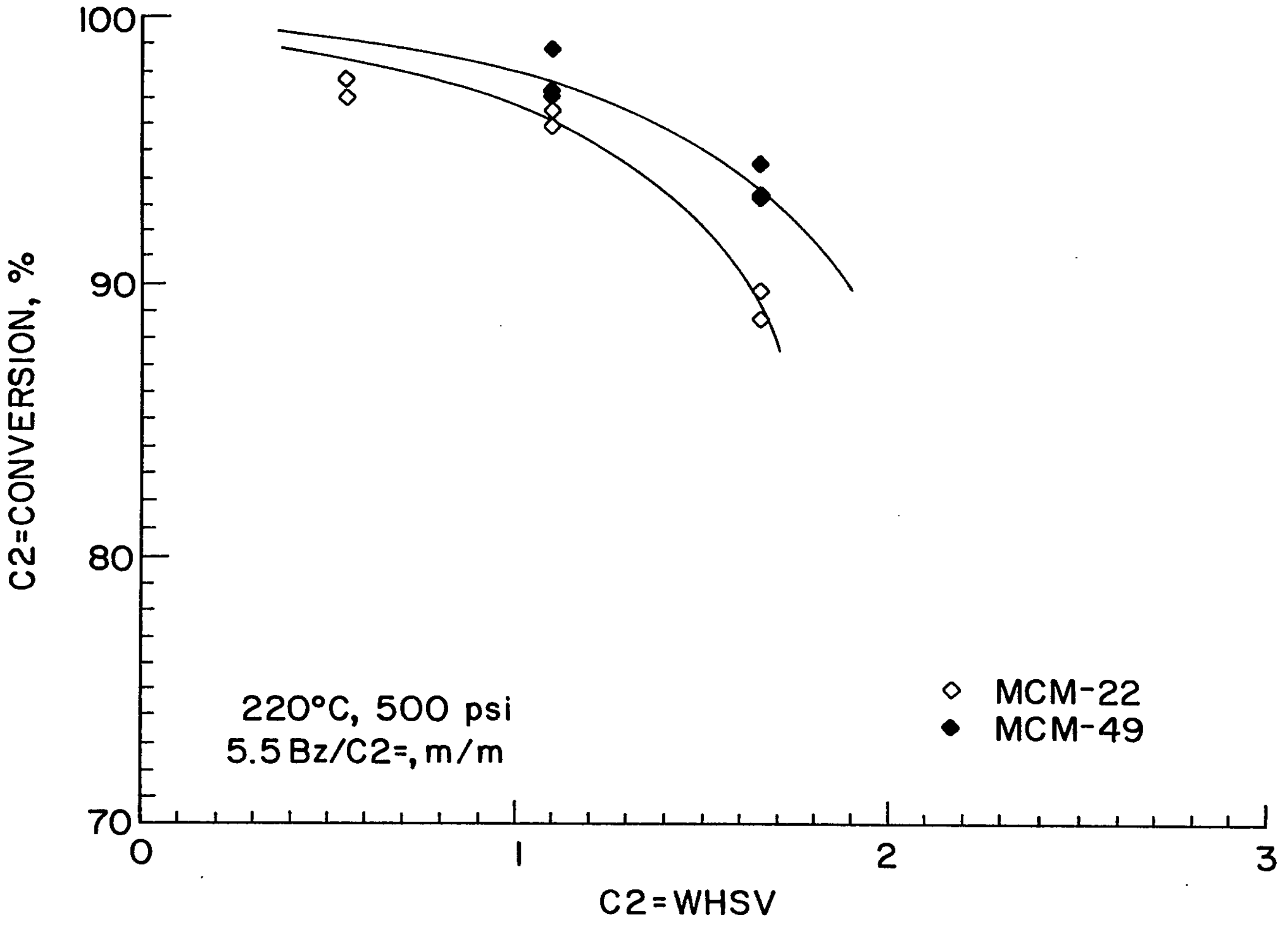
100
90
80
70
0
1
2
3
C2=CONVERSION, %
C2=WHSV
220°C, 500 psi
5.5 Bz/C2=, m/m
◇ MCM-22
◆ MCM-49

FIG. I

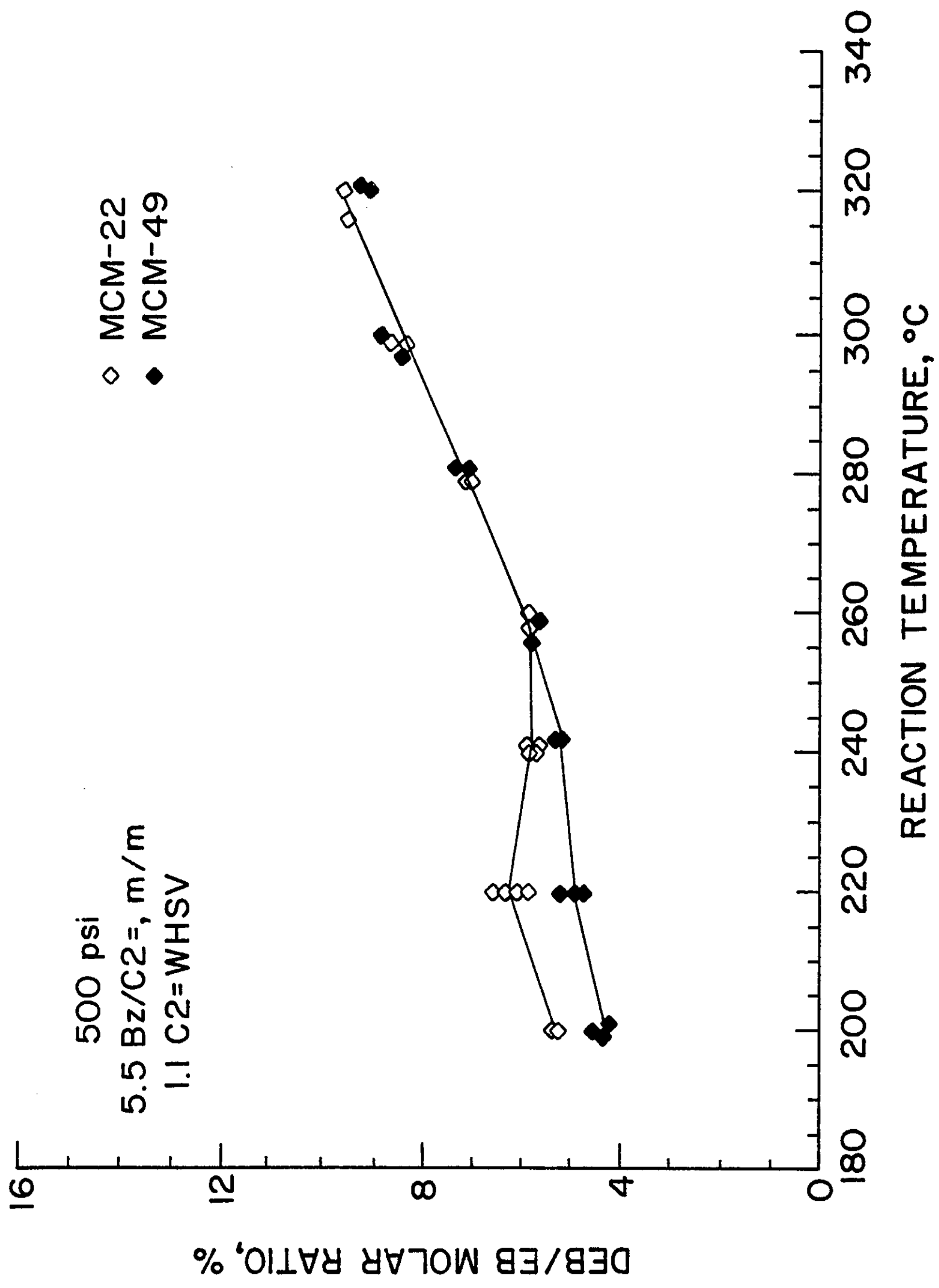
500 psi
5.5 Bz/C2=, m/m
1.1 C2=WHSV
◇ MCM-22
◆ MCM-49
DEB/EB MOLAR RATIO, %
0
4
8
12
16
180
200
220
240
260
280
300
320
340
REACTION TEMPERATURE, °C

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06710

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C07C 2/66
US CL : 585/446, 467
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/446, 467

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 5,196,623 (Butler) 23 March 1993, col. 3, lines 65-68 to col. 41 lines 1-16	1-3
A,P	US,A, 5,227,558 (Shamshoun et al) 13 July 1993; col. 2, lines 30-68	1-3
Y,P	US,A, 5,236,575 (Bennett et al), 17 August 1993; col. 2, lines 30-50, col. 6, lines 35-40.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search

15 SEPTEMBER 1994

Date of mailing of the international search report

05 OCT 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
ANTHONY MCFARLANE
Telephone No. (703) 308-3806