



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 1/00	A1	(11) International Publication Number: WO 99/51548 (43) International Publication Date: 14 October 1999 (14.10.99)
<p>(21) International Application Number: PCT/US99/07311</p> <p>(22) International Filing Date: 1 April 1999 (01.04.99)</p> <p>(30) Priority Data: 09/055,486 6 April 1998 (06.04.98) US</p> <p>(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).</p> <p>(72) Inventors: BROWN, Stephen, Harold; 20 Fairview Avenue, Princeton, NJ 08540 (US). GREEN, Larry, Arthur; 708 Union Road, Mickleton, NJ 08056 (US). MATHIAS, Mark, Fischer; 12 Ryder Cup Circle, Pittsford, NY 14534 (US). OLSON, David, Harold; 11 Morningside Drive, Pennington, NJ 08534 (US). SHINNAR, Reuel; 110 Ash Drive, Great Neck, NY 11021 (US). WARE, Robert, Adams; 8055 Stenton Avenue, Wyndmoor, PA 19038 (US). WEBER, William, Alois; 27 Hearthstone Lane, Marlton, NJ 08053 (US).</p> <p>(74) Agents: ROBERTS, Peter, W. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).</p>		<p>(81) Designated States: AU, AZ, BR, CA, CN, ID, IN, JP, KR, KZ, MX, NO, RU, SG, TM, UZ, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: PROCESS FOR PRODUCING LIGHT OLEFINS</p> <p>(57) Abstract</p> <p>There is provided a process for converting methanol and/or dimethyl ether to a product containing C₂-C₄ olefins which comprises the step of contacting a feed which contains methanol and/or dimethyl ether with a catalyst comprising a porous crystalline material, the contacting step being conducted in the presence of a co-fed aromatic compound under conversion conditions including a temperature of 350 to 480 °C and a methanol partial pressure in excess of 10 psia (70 kPa), the porous crystalline material having a pore size greater than the critical diameter of the aromatic compound and the aromatic compound being capable of alkylation by the methanol and/or dimethyl ether under the conversion conditions.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

PROCESS FOR PRODUCING LIGHT OLEFINS

The present invention relates to a process for producing light olefins rich in ethylene from methanol and dimethyl ether.

5 A remarkable growth in the production of synthetic fibers, plastics and rubber has taken place in recent decades. This growth, to a very large extent, has been supported and encouraged by an expanding supply of inexpensive petrochemical raw materials such as ethylene, propylene, and other, four and five carbon olefins. Side by side with this growth, there has been an increasing demand for alkylate, made by reacting olefins with
10 isobutane, for use as a high octane gasoline component.

Burgeoning demand for olefins, particularly ethylene, propylene and butenes, has of course led to periods of shortage which has led to substantial price increases in the feedstocks to the commercialized technologies. These feedstocks are largely C₂ - C₄ paraffins co-produced with natural gas and/or paraffinic straight run naphtha. These
15 feedstocks can be substantially more expensive than methane, making it desirable to provide efficient means for converting methane to olefins.

Conversion of methane to methanol followed by conversion of methanol to light olefins is among the most economic routes to make light olefins from methane. In this respect, it is known that methanol or methyl ether can be catalytically converted to olefin-
20 containing hydrocarbon mixtures by contact under certain conditions with particular types of crystalline zeolite materials. U.S. Patent Nos. 4,025,575 and 4,038,889, for example, both disclose processes whereby methanol and/or methyl ether can be converted to an olefin-containing product over a Constraint Index 1-12 zeolite catalyst, particularly ZSM-5. ZSM-5, in fact, converts methanol and/or methyl ether to hydrocarbons containing a
25 relatively high concentration of light olefins with prolonged catalyst lifetime before catalyst regeneration becomes necessary.

It has also been reported that other types of zeolite catalysts can be used to convert methanol and/or methyl ether to olefin-containing hydrocarbons products containing even higher proportions of light olefins than previously obtained with ZSM-5. For example, U.S.
30 Patent No. 4,079,095 discloses that zeolites of the erionite-offretite-chabazite type, and especially ZSM-34, can usefully be employed to promote conversion of methanol and/or methyl ether to products comprising a major amount of ethylene and propylene. However, while erionite-offretite-chabazite type catalysts are highly selective to light olefins production, such smaller pore zeolites tend to age rapidly in comparison to ZSM-5 when

used for methanol/methyl ether conversion.

U.S. Patent Nos. 4,677,242 and 4,752,651 disclose the conversion of methanol to C₂ - C₄ olefins over various silicoaluminophosphates and "non-zeolitic molecular sieves" (such as metal aluminophosphates) and teach that the addition of diluents, such as aromatic materials, having a kinetic diameter greater than the pore size of the molecular sieve increases the ethylene to propylene ratio in the product.

T. Mole, G. Bett, and D.J. Seddon, *Journal of Catalysis* 84, 435 (1983), disclose that the presence of aromatic compounds can accelerate the zeolite-catalyzed conversion of methanol to hydrocarbons. The article reports ethylene yields of 5 to 22% when methanol is catalytically converted in the presence of benzene or toluene over ZSM-5 at sub-atmospheric pressure, 279 to 350°C, and 100% methanol conversion.

U.S. Patent No 4,499,314 discloses that the addition of various promoters, including aromatic compounds, such as toluene, accelerate the conversion of methanol to hydrocarbons over zeolites, such as ZSM-5, which have a pore size sufficient to permit sorption and diffusion of the promoter. In particular, the '314 patent teaches that the increased conversion resulting from the addition of the promoter allows the use of lower severity conditions, particularly lower temperatures, which increase the yield of lower olefins (column 4, lines 17-22). Thus, in Example 1 of the patent, the addition of toluene as a promoter reduces the temperature required to achieve full methanol conversion from 295 to 288°C while increasing the ethylene yield from 11 to 18 wt.%. In the Examples of the '314 patent the methanol feedstock is diluted with water and nitrogen such that the methanol partial pressure is less than 2 psia.

In spite of the existence of methanol conversion processes utilizing a variety of zeolite catalysts and process conditions, there is a continuing need to develop new procedures suitable to convert an organic charge comprising methanol and/or dimethyl ether selectively to light olefin products and in particular ethylene. An object of the present invention is therefore to address this need.

The present invention resides in a process for converting methanol and/or dimethyl ether to a product containing C₂ - C₄ olefins which comprises the step of contacting a feed which contains methanol and/or dimethyl ether with a catalyst comprising a porous crystalline material, the contacting step being conducted in the presence of a co-fed aromatic compound under conversion conditions including a temperature of 350 to 480°C and a methanol partial pressure in excess of 10 psia (70 kPa), the porous crystalline material having a pore size greater than the critical diameter of the aromatic compound and

the aromatic compound being capable of alkylation by the methanol and/or dimethyl ether under the conversion conditions.

Preferably, the molar ratio of methanol and/or dimethyl ether to aromatic compound is greater than 5:1 and preferably is less than 300:1. More preferably, the molar ratio of methanol and/or dimethyl ether to aromatic compound is from 10:1 to 150:1.

Preferably, the conversion conditions include a temperature of 400 to 460°C.

Preferably, the conversion conditions are such that the methanol conversion rate is less than 90% and more preferably less than 80%.

Preferably, the porous crystalline material has a pore size between 5 and 7 Angstrom.

Preferably, the porous crystalline material is an aluminosilicate zeolite and most preferably is ZSM-5. Preferably, the catalyst has an alpha value less than 10 and more preferably less than 2.

Preferably, the porous crystalline material has a Diffusion Parameter for 2,2-dimethylbutane of 0.1 - 20 sec⁻¹ when measured at a temperature of 120°C and a 2,2-dimethylbutane pressure of 60 torr (8 kPa).

Preferably, the porous crystalline material has a Diffusion Parameter of 0.2-5 sec⁻¹.

Preferably, the catalyst contains coke or an oxide modifier selected from oxides of boron, magnesium, silicon and most preferably phosphorus.

Preferably, the catalyst contains 0.05 to 20 wt.%, and more preferably 1 to 10 wt.%, of the coke or the oxide modifier on an elemental basis.

The present invention provides a process for selectively converting methanol and/or dimethyl ether to C₂ - C₄ olefins, particularly ethylene, over a porous crystalline catalyst and in the presence of a co-fed aromatic compound co-feed which has a critical diameter less than the pore size of the catalyst and which is capable of alkylation by the methanol and/or dimethyl ether under the conditions of the conversion. The process of the present invention is distinguished from that of U.S. Patent No. 4,499,314 discussed above in that a substantially water-free methanol feed is contacted with a zeolite catalyst, such as ZSM-5, in the presence of a reactive aromatic compound at a relatively high temperature of 350°C to 480°C and a relatively high methanol partial pressure in excess of 10 psia (70 kPa). The methanol can contain various amounts of water but, unlike other processes, steam co-feed is not necessary and has no deleterious effect. In addition, the process conditions are preferably controlled so that the methanol conversion is less than 90% and more preferably less than 80%. In this way it is found that ethylene selectivities in excess of 30 wt.% can be

achieved as compared to the ethylene selectivities of 18 - 25% by weight reported in the '314 patent.

While not wishing to be bound by any theory of operation, the ethylene selectivity of the process of the invention is believed to follow from our observation that virtually all the ethylene produced via the catalytic partial conversion of methanol to light olefins using zeolite catalysts is derived from the back-cracking of ethyl-aromatic intermediates. The formation of such ethyl-aromatic intermediates is believed to be facilitated in the present process by a mechanism in which the aromatic compound effectively acts as a catalyst in the conversion of two molecules of methanol to one molecule of ethylene. Thus the methylation of aromatics with methanol in zeolites, such as ZSM-5, is a well-known, rapid reaction. The product polymethylbenzenes are stable but are too large to easily exit the pores of the catalyst. Although relatively slow, the next expected reaction of a polymethyl aromatic is skeletal isomerization to a mixed methyl-ethyl aromatic. Once formed, ethyl aromatics are prone to a rapid cracking reaction to form ethylene and the co-catalytic aromatic ring.

In the process described in U.S. Patent No. 4,499,314, the toluene co-feed is merely a promoter to initiate the reaction. When methanol is converted over the same catalyst at 288°C in the absence of or in the presence of toluene, there is little difference in the ethylene selectivity obtained. Additionally, a process utilizing the same catalyst as that used in U.S. Patent No 4,499,314, operating at the same temperature (288 - 295°C), at high pressure (90 psia), and >50% methanol conversion produces little or no olefins. In contrast, the process of the invention unexpectedly maintains nearly constant ethylene selectivity at 80% methanol conversion out to reactor pressures approaching 100 psia.

In addition the invention described here unexpectedly shows that co-feed aromatics can be used as a novel control handle for ethylene yield. Increasing the amount of co-feed aromatics from 0 to 5 wt.% increases the selectivity to ethylene at constant conditions and conversion. Because only a small amount is required, using an aromatic co-feed as a control handle is easily accomplished at low cost to the operator.

Any methanol feed comprising at least 60 wt.% of methanol may be used to provide methanol for the use in this invention. Substantially pure methanol, such as industrial grade anhydrous methanol, is eminently suitable. Crude methanol, which usually contains from 12 to 20 wt.% water, or even a more dilute solution, may also be used. However, the presence of water as a diluent to reduce the methanol partial pressure is not required. Trace amounts (< 1% by weight) of non-aromatic organic impurities, such as higher

alcohols, aldehydes, or other oxygenated compounds have little effect on the conversion reaction of this invention and may be present in the methanol feed.

In place of, or in addition to methanol, the non-aromatic reactant feed may comprise dimethyl ether. When this component is present, it can comprise up to 100% of the non-aromatic organic reactant feed or dimethyl ether can be admixed with methanol to form the non-aromatic reactant feed. For purposes of the present invention, it is contemplated to directly convert methanol and/or methyl ether in the feed to a hydrocarbon mixture characterized by a high content of light olefins, especially ethylene. Such amounts of dimethyl ether as may be formed concomitantly in the conversion reaction, however, may be recovered and recycled with fresh organic reactant feed.

The aromatic co-feed can come from a wide variety of sources and even substantial amounts of non-aromatic organic components have little impact on the catalytic role of the aromatic co-feed. For this reason, any organic feedstream containing >10 wt.% aromatics, which have a critical diameter less than the pore size of the catalyst so as to be able to easily diffuse into the catalyst pores, is suitable for use as the aromatic co-feed in the process of the invention. These include, but are not limited to, benzene, toluene, xylenes, C₉+ reformat streams, light reformates, full-range reformates or any distilled fraction thereof, coker naphtha or any distilled fraction thereof, FCC naphtha or any distilled fraction thereof, and coal derived aromatics. Part of the required aromatic compound can also be produced in-situ by aromatization of the methanol feed. The presence of impurities, such as nitrogen and sulfur compounds, dienes and styrenes, in the aromatic component can be tolerated with little impact when fluid or moving bed embodiments of the invention are employed.

In a preferred embodiment, toluene comprises some or all of the aromatic portion of the feedstock.

The molar ratio of methanol and/or dimethyl ether to aromatic compound will normally be greater than 5:1, since higher concentrations of aromatic compound lead to excessive coking, increased volumes of separation and recycle traffic and minimal gains in total chemical selectivities. Moreover the molar ratio of methanol and/or dimethyl ether to aromatic compound is normally maintained below 300:1, since lower concentrations of aromatic compound lead to little or no noticeable improvement in the ethylene selectivity of the process. However, the amount of aromatic compound required decreases as the pressure increases so that at high pressure it may be possible to achieve a significant improvement in ethylene selectivity with molar ratios of methanol and/or dimethyl ether to

aromatic compound above 300:1. Preferably the molar ratio of methanol and/or dimethyl ether to aromatic compound is from 5:1 to 250:1.

The catalyst employed in the process of the invention is a porous crystalline material which has a pore size greater than the critical diameter of the aromatic compound co-feed.

5 Preferred catalysts are porous crystalline materials having a pore size between 5 and 7 Angstrom and in particular intermediate pore size, aluminosilicate zeolites. One common definition for intermediate pore zeolites involves the Constraint Index test which is described in U.S. Patent No. 4,016,218. In this case, intermediate pore zeolites have a Constraint Index of 1-12, as measured on the zeolite alone without the introduction of
10 modifiers and prior to any treatment to adjust the diffusivity of the catalyst. In addition to the medium-pore size aluminosilicates, other medium pore acidic metallocates, such as silicoaluminophosphates (SAPOs), can be used in the process of the invention.

Particular examples of suitable medium pore zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, and MCM-22, with ZSM-5 and ZSM-11 being
15 particularly preferred.

Zeolite ZSM-5 and the conventional preparation thereof are described in U.S. Patent No. 3,702,886. Zeolite ZSM-11 and the conventional preparation thereof are described in U.S. Patent No. 3,709,979. Zeolite ZSM-12 and the conventional preparation thereof are described in U.S. Patent No. 3,832,449. Zeolite ZSM-23 and the conventional
20 preparation thereof are described in U.S. Patent No. 4,076,842. Zeolite ZSM-35 and the conventional preparation thereof are described in U.S. Patent No. 4,016,245. ZSM-48 and the conventional preparation thereof is taught by U.S. Patent No. 4,375,573. MCM-22 is disclosed in U.S. Patent Nos. 5,304,698; 5,250,277; 5,095,167; and 5,043,503.

In order to increase the concentration of aromatics in the catalyst pores without
25 increasing the aromatic to methanol molar ratio, it may be desirable to use a catalyst having increased diffusional barriers. In particular, it may be desirable to employ a catalyst which comprises a porous crystalline material having a Diffusion Parameter for 2,2-dimethylbutane of $0.1-20 \text{ sec}^{-1}$, preferably $0.1-15 \text{ sec}^{-1}$ and most preferably $0.2-5 \text{ sec}^{-1}$ when measured at a temperature of 120°C and a 2,2-dimethylbutane pressure of 60 torr (8 kPa).

30 As used herein, the Diffusion Parameter of a particular porous crystalline material is defined as $D/r^2 \times 10^6$, wherein D is the diffusion coefficient (cm^2/sec) and r is the crystal radius (cm). The required diffusion parameters can be derived from sorption measurements provided the assumption is made that the plane sheet model describes the diffusion process. Thus for a given sorbate loading Q, the value Q/Q_∞ , where Q_∞ is the equilibrium

sorbate loading and is mathematically related to $(Dt/r^2)^{1/2}$ where t is the time (sec) required to reach the sorbate loading Q . Graphical solutions for the plane sheet model are given by J. Crank in "Mathematics of Diffusion", Oxford University Press, Ely House, London, 1967.

The intermediate pore zeolites described above as being preferred for the process
5 of the invention may have Diffusion Parameter values in excess of the required 0.1 - 20 sec^{-1} range. However, the Diffusion Parameter can be controlled or modified to the required value by a variety of methods. For example, the required diffusivity can be achieved by using large crystal forms (greater than 1 micron) of the porous crystalline material, by depositing coke on the material prior to use in the process (as described in
10 U.S. Patent No. 4,097,543) and/or by combining the material with at least one oxide modifier, preferably selected from the group consisting of oxides of boron, magnesium, calcium, silicon, lanthanum and most preferably phosphorus. The total amount of coke or oxide modifier, as measured on an elemental basis, may be between 0.05 and 20 wt.%, and preferably is between 1 and 10 wt.%, based on the weight of the final catalyst.

15 Alternatively, the required diffusional constraint can be achieved by severely steaming the catalyst so as to effect a controlled reduction in the micropore volume of the catalyst to not less than 50%, and preferably to 50 to 90%, of that of the unsteamed catalyst. Reduction in micropore volume is derived by measuring the n-hexane adsorption capacity of the catalyst, before and after steaming, at 90°C and 75 torr n-hexane pressure.
20 Steaming of the porous crystalline material is effected at a temperature of at least 850°C, preferably 950 to 1075°C, and most preferably 1000 to 1050°C for 10 minutes to 10 hours, preferably from 30 minutes to 5 hours. To effect the desired controlled reduction in diffusivity and micropore volume, it may be desirable to combine the porous crystalline material, prior to steaming, with a phosphorus modifier. The total amount of phosphorus
25 modifier, which will normally be present in the catalyst in oxide form, as measured on an elemental basis, may be between 0.05 and 20 wt.%, and preferably is between 1 and 10 wt.%, based on the weight of the final catalyst.

Where the modifier is phosphorus, incorporation of modifier in the catalyst of the invention is conveniently achieved by the methods described in U.S. Patent Nos.
30 4,356,338; 5,110,776; and 5,231,064. Similar techniques known in the art can be used to incorporate other modifying oxides into the catalyst of the invention.

The porous crystalline material employed in the process of the invention may be combined with a variety of binder or matrix materials resistant to the temperatures and other conditions employed in the process. Such materials include active and inactive

materials such as clays, silica and/or metal oxides such as alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material that is active tends to change the conversion and/or selectivity of the catalyst and hence is generally not preferred. Inactive materials
5 suitably serve as diluents to control the amount of conversion in a given process 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. Said materials, i.e., clays, oxides, etc., function as
10 binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay and/or oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

Naturally occurring clays which can be composited with the porous crystalline
15 material include the montmorillonite and kaolin family, which families include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

20 In addition to the foregoing materials, the porous crystalline material can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia silica-alumina-magnesia and silica-magnesia-zirconia.

25 The relative proportions of porous crystalline material and inorganic oxide matrix vary widely, with the content of the former ranging from 1 to 90% by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 wt.% of the composite.

Preferably, the binder material comprises silica or a kaolin clay.

30 Procedures for preparing silica-bound zeolites, such as ZSM-5, are described in U.S. Patent Nos. 4,582,815; 5,053,374; and 5,182,242. A particular procedure for binding ZSM-5 with a silica binder involves an extrusion process.

The porous crystalline material may be combined with a binder in the form of a fluidized bed catalyst. This fluidized bed catalyst may comprise clay in the binder thereof,

and may be formed by a spray-drying process to form catalyst particles having a particle size of 20 - 200 microns.

The catalyst employed of the invention preferably has a very low acid activity. Using the alpha test of acid activity disclosed in *Journal of Catalysis*, volume 61, page 395
5 (1980), the catalyst of the invention preferably has an alpha value less than 10, more preferably less than 2.

The process of the invention is preferably carried out in a moving or fluid catalyst bed with continuous oxidative regeneration. The extent of coke loading can then be continuously controlled by varying the severity and/or the frequency of regeneration.

10 The process of the present invention is conducted at a relatively high temperature between 350 and 500°C, preferably between 400 and 480°C, since, as will be illustrated by the following Examples and contrary to the teaching in U.S. Patent No. 4,499,314, we have found that such a temperature range is critical to the selective production of lower olefins. While not wishing to be bound by any theory of operation, we believe that such a relatively
15 high temperature is essential to the skeletal isomerization and cracking of the polymethylbenzene intermediates produced, whereas higher temperatures lead to excessive coking.

The process of the invention is advantageous in that it is found that the lower olefin selectivity of the product is generally independent of methanol partial pressure so that the
20 necessity in prior art processes to reduce the methanol pressure by the addition of diluents or by operation at reduced pressure can be avoided. The ability to operate at higher methanol partial pressures also allows the absolute yield per pass of olefin product to be increased. A suitable methanol partial pressure for use in the process of the invention is in excess of 10 psia (70 kPa), preferably 15 to 150 psia.

25 In addition, it is desirable that the conversion conditions are controlled so that the methanol conversion level is less than 90% and preferably less than 80% since, at higher conversion levels, competing reactions to aromatics methylation, such as olefin alkylation and/or oligomerization to produce C₅+ isoolefins and/or olefin conversion to aromatics and paraffins, lower the selectivity to ethylene and propylene. Suitable control of the methanol
30 conversion can, of course, be achieved by variation of the weight hourly space velocity, which typically can vary between 0.1 and 100, preferably between 0.1 and 10.

The process of the invention converts methanol and/or dimethyl ether to a light olefin stream in which ethylene comprises over 40 wt.%, and typically over 50 wt.%, of the C₂ - C₄ olefins and in which ethylene comprises more than 90 wt.%, preferably more than

95 wt.%, of the C₂ component. In addition to the light olefins, a product of the process is xylenes comprising a high proportion of the para isomer, particularly where a diffusionally constrained catalyst is employed as described above.

The invention will now be more particularly described in the following Examples and the accompanying drawings in which:

Figure 1 is a graph plotting ethylene selectivity against methanol conversion for the catalyst of Example 1 when used to convert methanol in the presence of varying amounts of water and toluene;

Figure 2 is a graph comparing the ethylene selectivity with temperature for the catalyst of Example 1 when used to convert methanol in the presence of toluene at methanol to toluene molar ratios of 10:1 and 155:1;

Figures 3 and 4 are graphs similar to Figure 3 but comparing the toluene conversion and wt.% ethylene/p-xylene, respectively, with temperature using the same catalyst and methanol to toluene molar ratios; and

Figure 5 is a graph comparing ethylene selectivity with methanol conversion for the catalyst of Example 1 at a methanol to toluene molar ratio of 55:1 with that for the catalyst of Example 4 at a methanol to toluene molar ratio of 26:1.

Figure 6 is a graph comparing olefin selectivity with temperature at methanol partial pressures of 15 and 90 psia for the catalyst of Example 5.

Figure 7 is a graph comparing the effects of methanol partial pressure on olefin selectivity at different temperatures using the catalyst of Example 5.

In the Examples, micropore volume (n-hexane) measurements were made on a computer controlled (Vista/Fortran) duPont 951 Thermalgravimetric analyzer. Isotherms were measured at 90°C and adsorption values taken at 75 torr n-hexane. The diffusion measurements were made on a TA Instruments 2950 Thermalgravimetric Analyzer equipped with a Thermal Analysis 2000 controller, a gas switching accessory and an automatic sample changer. Diffusion measurements were made at 120°C and 60 torr 2,2-dimethylbutane. Data were plotted as uptake versus square root of time. Fixed bed catalytic testing was conducted using a 3/8" (1 cm) outside diameter, down-flow reactor using equipped with a thermocouple. Methanol, water, and aromatics were all pumped to the reactor by way of a vaporizer equipped with a static mixer to thoroughly gassify and mix the feedstocks upstream of the reactor. The reactor was equipped with a backpressure regulator to enable examination of the products at a wide variety of temperature, pressures and WHSV's. The total reactor effluent was analyzed, on line, by gas chromatography.

Methanol conversion was calculated based on hydrocarbon formation only. Selectivities to hydrocarbon product were calculated on a "water free" basis.

Example 1

Phosphoric acid, kaolin clay, and 450:1 SiO₂/Al₂O₃ ZSM-5 were slurried in water
5 and spray dried to make a typical fluid-bed catalyst. The catalyst was calcined in air at 510°C. The finished catalyst contained 40 wt.% ZSM-5 and 4.5 wt.% phosphorus. This material has an n-hexane sorption of 33.5, a diffusion parameter of 27, and an alpha of 7. The catalyst was then steamed at 1050°C for 0.75 hours in 1 atmosphere steam to produce a final catalyst having a Diffusion Parameter of 0.46 sec⁻¹ and an n-hexane sorption of 30.6
10 mg/g.

Example 2

A first 0.5 gm sample of the steamed catalyst of Example 1 was used to convert a pure methanol feedstock at 0.5 to 10 WHSV, 430°C, and 1 atm pressure. A wide range of methanol conversions was obtained. The hydrocarbon product ethylene selectivity is
15 plotted vs. methanol conversion in Figure 1.

A second 0.5 gm sample of the steamed catalyst of Example 1 was used to convert a 3:1 molar methanol: water feedstock at 0.5 to 10 WHSV, 430°C, and 1 atm pressure. A wide range of methanol conversions was obtained. The hydrocarbon product ethylene selectivity is plotted against methanol conversion in Figure 1.

20 A third 0.5 gm sample of the steamed catalyst of Example 1 was used to convert a 26:1 molar methanol: toluene feedstock at 0.5 to 5 WHSV, 430°C, and 1 atm pressure. A wide range of methanol conversions was obtained. The hydrocarbon product ethylene selectivity is plotted against methanol conversion in Figure 1.

A fourth 0.5 gm sample of the steamed catalyst of Example 1 was used to convert a
25 3:1 molar methanol: toluene feedstock at 0.5 to 5 WHSV, 430°C, and 1 atm pressure. A wide range of methanol conversions was obtained. The hydrocarbon product ethylene selectivity is plotted against methanol conversion in Figure 1.

Figure 1 clearly demonstrates that addition of one mole of steam for each 3 moles of methanol to the feedstock leads to a negligible change in ethylene selectivity. In
30 contrast, the addition of toluene in amount as little as 1 mole of toluene for 26 moles of methanol leads to a large improvement in ethylene selectivity, particularly if the methanol conversion is maintained below 90%.

Example 3

A further 0.5 gm sample of the steamed catalyst of Example 1 was used to convert a 12:1 molar methanol: toluene feedstock at 1 atm pressure, 0.5 to 5 WHSV and various temperatures between 380 and 480°C. A wide range of methanol conversions was
5 obtained. From this data the ethylene selectivity, toluene conversion, and wt.% ethylene/p-xylene at 70% methanol conversion were extracted at each temperature and the results are plotted in Figures 2 to 4. The test was then repeated with a feedstock having a 155:1 methanol: toluene molar ratio and again the data is plotted in Figures 2 to 4.

Figures 2 to 4 demonstrate that the 155:1 methanol:toluene feedstock does not
10 have enough aromatic co-feed at any temperature to produce as much ethylene as 12:1 methanol:toluene feedstock. Moreover, as the temperature rises, the ethylene selectivity decreases rapidly with the 155:1 methanol:toluene feed. Figures 2 to 4 also show that for the 12:1 methanol:toluene feedstock ethylene selectivity is constant with temperature but the ratio of ethylene:p-xylene in the product decreases rapidly with increasing temperature.
15 Thus control of catalyst, feed, and temperatures enables a producer to choose from among a wide range of product ethylene:p-xylene ratios.

Example 4

A sample of the phosphorus-treated, unsteamed catalyst from Example 1 was steamed at 870°C for 6 hours in 1 atmosphere steam to produce a catalyst having a
20 Diffusion Parameter of 31 sec^{-1} and an n-hexane sorption of 34.9 mg/g. 0.5 gm of this catalyst was used to convert a 26:1 molar methanol:toluene feedstock at 0.5 to 10 WHSV, 430°C, and 1 atm pressure. A wide range of methanol conversions was obtained and ethylene selectivity of the hydrocarbon product is plotted vs. methanol conversion in Fig. 5.

By way of comparison, a further sample of the steamed catalyst of Example 1 was
25 used to convert a 55:1 molar methanol: toluene feedstock under the same conditions and again ethylene selectivity is plotted vs. methanol conversion is plotted in Figure 5.

Figure 5 demonstrates the relationship between the amount of aromatic co-feed and the diffusivity of the catalyst. The 55:1 feed data with the diffusion restricted catalyst of Example 1 is essentially the same as the 26:1 molar feed data with the less diffusion
30 restricted catalyst of Example 4. This shows that less aromatic co-feed is required to achieve a given product distribution with a more diffusion restricted catalyst than is required with a less diffusion restricted catalyst.

Example 5

A commercially available FCC additive catalyst, containing 25 wt.% ZSM-5 with a silica to alumina molar ratio of 26:1 and 3 wt.% phosphorus, was used in this Example. The catalyst had been pre-steamed at 1450°F (790°C) for 4 hours and had an alpha value of 3,
5 a Diffusion Parameter of 25 and an n-hexane sorption of 25 mg/g. The catalyst was used to convert a mixture of 90 wt.% methanol and 10 wt.% toluene (methanol:toluene molar ratio of 26:1) at methanol partial pressures of 15 psia (103 kPa) and 90 psia (620 kPa) and at a methanol conversion level of 80%. Various temperatures between 210 and 490°C were used and the results are plotted in Figure 6. From Figure 6, it will be seen that the
10 conversion of methanol in the presence of toluene is highly selective to olefins at temperatures between 350 and 480°C and that the olefin selectivity is generally independent of methanol partial pressure especially at temperatures 400 and 450°C.

Example 6 (Comparative)

An alumina-bound ZSM-5 catalyst, containing 65 wt.% ZSM-5 with a silica to
15 alumina molar ratio of 26:1, which had been steamed at 515°C for 1 hour was used in this Example. The catalyst had an alpha value of 100, a Diffusion Parameter of 1000 and an n-hexane sorption of 77 mg/g. The catalyst was used convert (a) a mixture of 90 wt.% methanol and 10 wt.% toluene (methanol:toluene molar ratio of 26:1) and (b) pure methanol at a temperature of 270°C and a methanol conversion level of 50% and the
20 results are listed in Table 1. From Table 1 it will be seen that at this low temperature the light olefin yield is marginally less with the toluene co-feed than with the pure methanol feed.

Table 1

	Run (a)	Run (b)
BedTemp, °C	263	262
Furnace T	260	265
WHSV	0.3	0.7
TOS, min	120	63
Feed Comp., wt. %		
Methanol/DME	90.000	100.000
Toluene	10.000	0.000
	100.000	100.000
Product Comp., wt. %		
Methane	0.275	0.330
Ethylene	3.167	4.170
Ethane	0.081	0.056
Propylene	1.929	2.483
Propane	1.362	1.730
Methanol/DME	43.438	42.644
Butenes	1.211	1.473
Butanes	1.388	1.956
C ₅ - C ₉ nonA	4.014	5.503
Isopentane	1.504	2.309
Benzene	0.000	0.000
Heptane	0.000	0.000
Toluene	4.538	0.106
EB	0.023	0.029
M+p-xylene	2.141	1.220
o-xylene	1.823	0.159
p-ethyltoluene	0.313	0.334
1,2,4 TMB	2.543	1.382
C ₁₀ ⁺	3.951	1.748
Water	26.300	32.369
	100.000	100.000
Methanol Conversion	51.7	57.4
Methanol to :		
Ethylene	14.2%	15.5%
Propylene	8.7%	9.3%
Butenes	5.4%	5.5%
C ₅ - C ₉ nonA	24.8%	29.1%
C ₁ - C ₄ Paraffins	14.0%	15.2%
Feedstock	10.9%	0.0%
New rings	21.9%	25.4%
Total olefins	28.4%	30.3%

Example 7

The catalyst of Example 5 was used to convert a mixture of 90 wt.% methanol and 10 wt.% toluene (methanol:toluene molar ratio of 26:1) at various temperatures and pressures. The total olefin selectivity under each condition at a methanol conversion level of 80% are shown in Figure 7. The figure clearly shows that at lower temperatures the effect of pressure on total olefin selectivity becomes more and more pronounced. Additionally, these results reemphasize that total olefin selectivity is a strong function of temperature.

CLAIMS:

1. A process for converting methanol and/or dimethyl ether to a product containing C₂ - C₄ olefins which comprises the step of contacting a feed which contains
5 methanol and/or dimethyl ether with a catalyst comprising a porous crystalline material, the contacting step being conducted in the presence of a co-fed aromatic compound under conversion conditions including a temperature of 350 to 480°C and a methanol partial pressure in excess of 10 psia (70 kPa), the porous crystalline material having a pore size greater than the critical diameter of the aromatic compound and the aromatic compound
10 being capable of alkylation by the methanol and/or dimethyl ether under the conversion conditions.
2. The process of claim 1 wherein the molar ratio of methanol and/or dimethyl ether to aromatic compound is greater than 5:1 and less than 300:1.
15
3. The process of claim 1 wherein the molar ratio of methanol and/or dimethyl ether to aromatic compound is from 5:1 to 250:1.
4. The process of claim 1 wherein the aromatic compound is selected from the
20 group consisting of benzene, toluene, xylenes, C₉+ reformat streams, light reformates, full-range reformates or any distilled fraction thereof, coker naphtha or any distilled fraction thereof, FCC naphtha or any distilled fraction thereof, and coal derived aromatics.
5. The process of claim 1 wherein the conversion conditions include a
25 temperature of 400 to 480°C.
6. The process of claim 1 wherein the conversion conditions are such that the methanol conversion rate is less than 90%.
- 30 7. The process of claim 1 wherein the porous crystalline material has a pore size between 5 and 7 Angstrom.
8. The process of claim 1 wherein the porous crystalline material is ZSM-5.

9. The process of claim 1 wherein the porous crystalline material has a Diffusion Parameter for 2,2-dimethylbutane of $0.1 - 20 \text{ sec}^{-1}$ when measured at a temperature of 120°C and a 2,2-dimethylbutane pressure of 60 torr (8 kPa).
- 5 10. The process of claim 1 wherein the catalyst has an alpha value less than 10.

1/4

FIG. 1

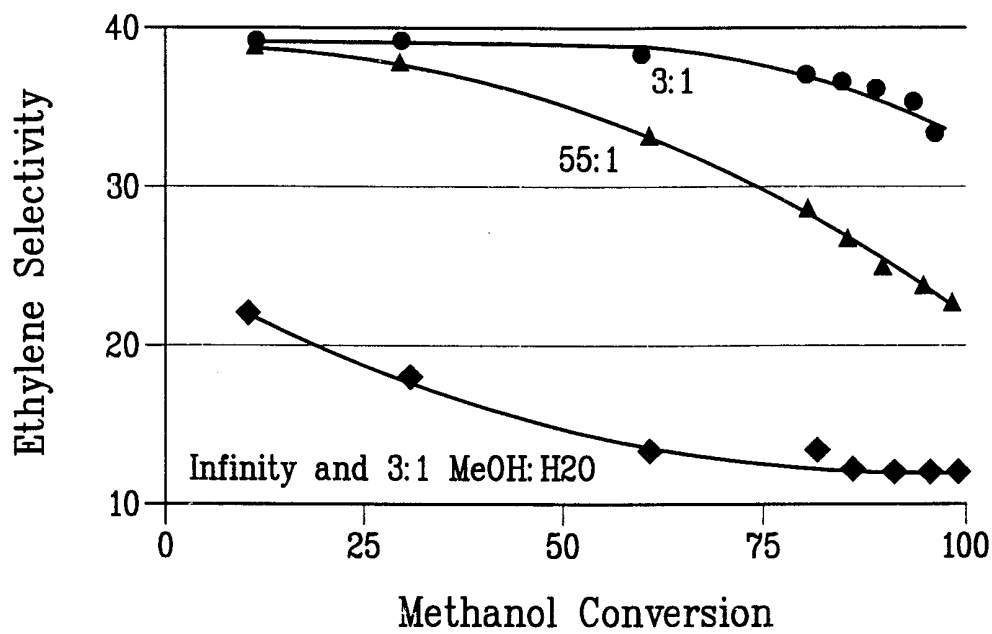


FIG. 2

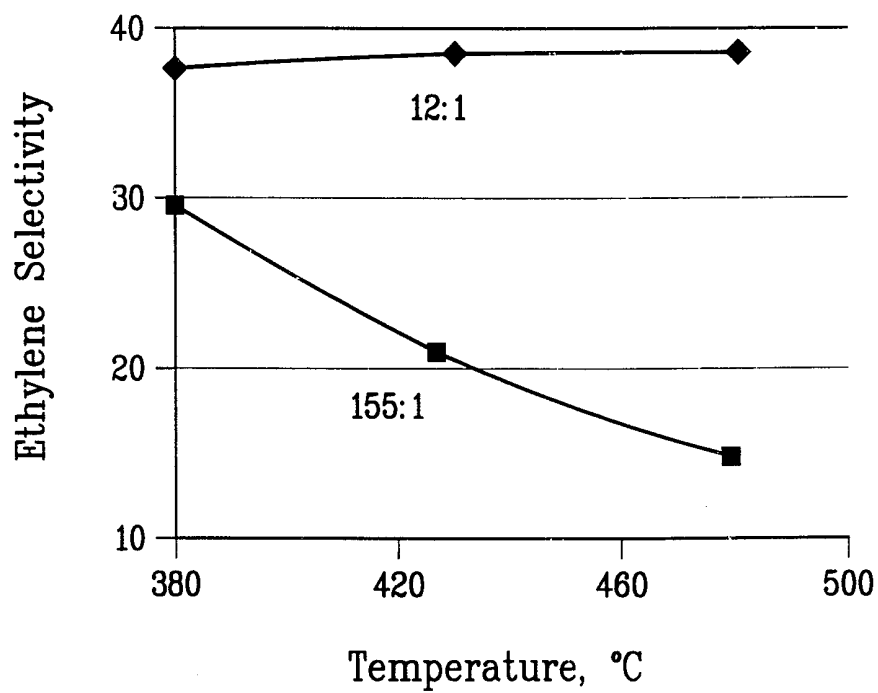


FIG. 3

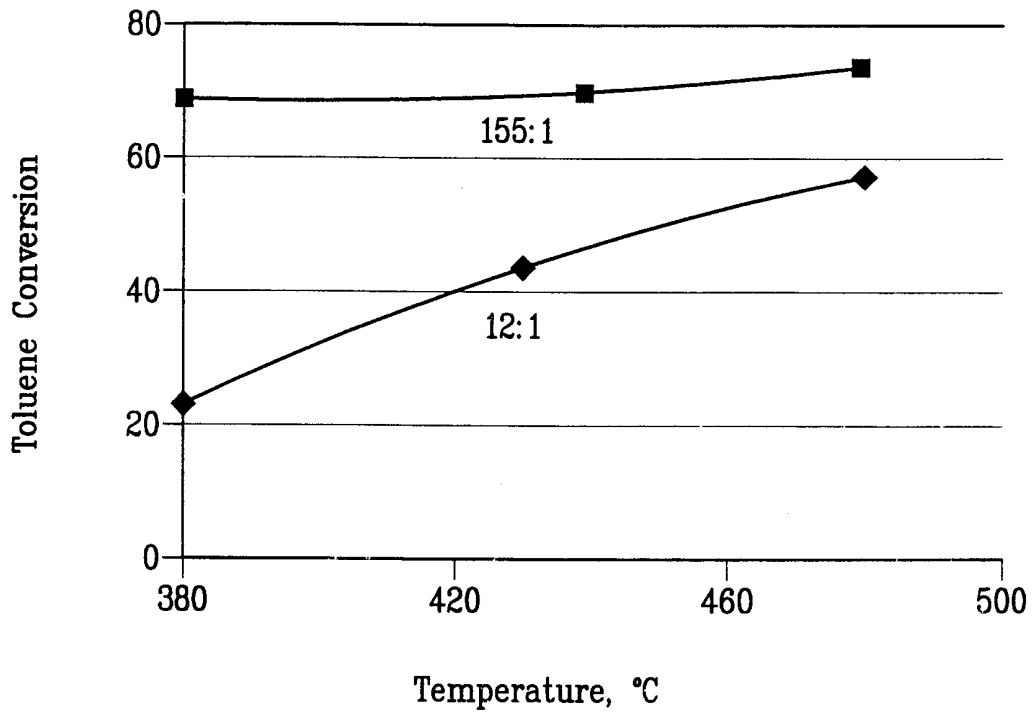
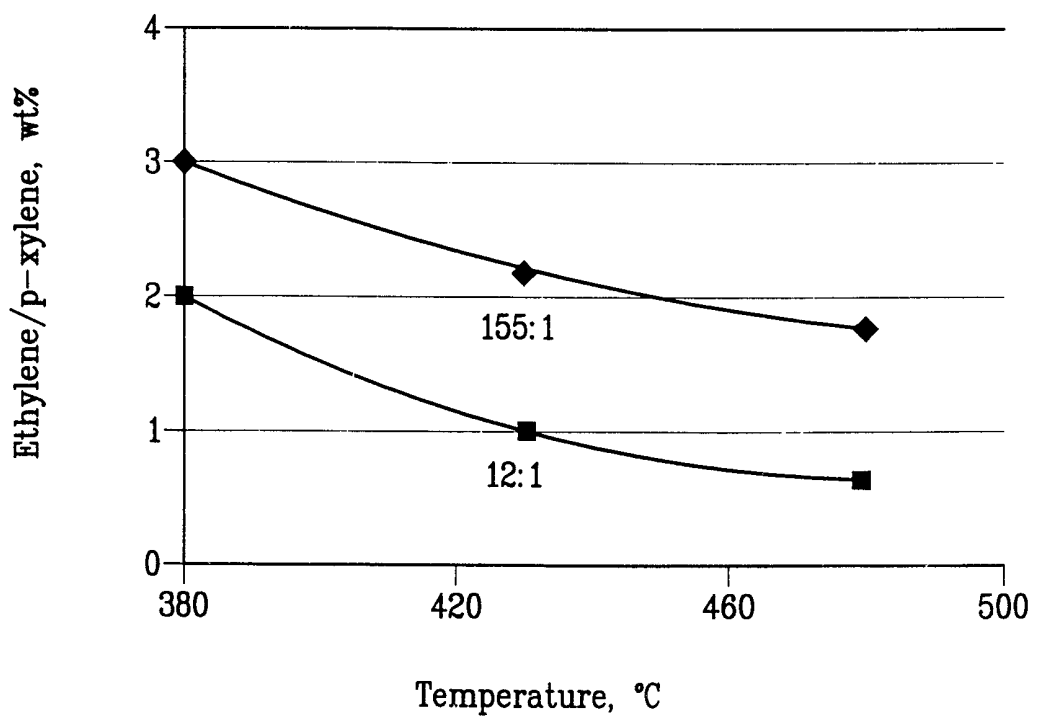


FIG. 4



3/4

FIG. 5

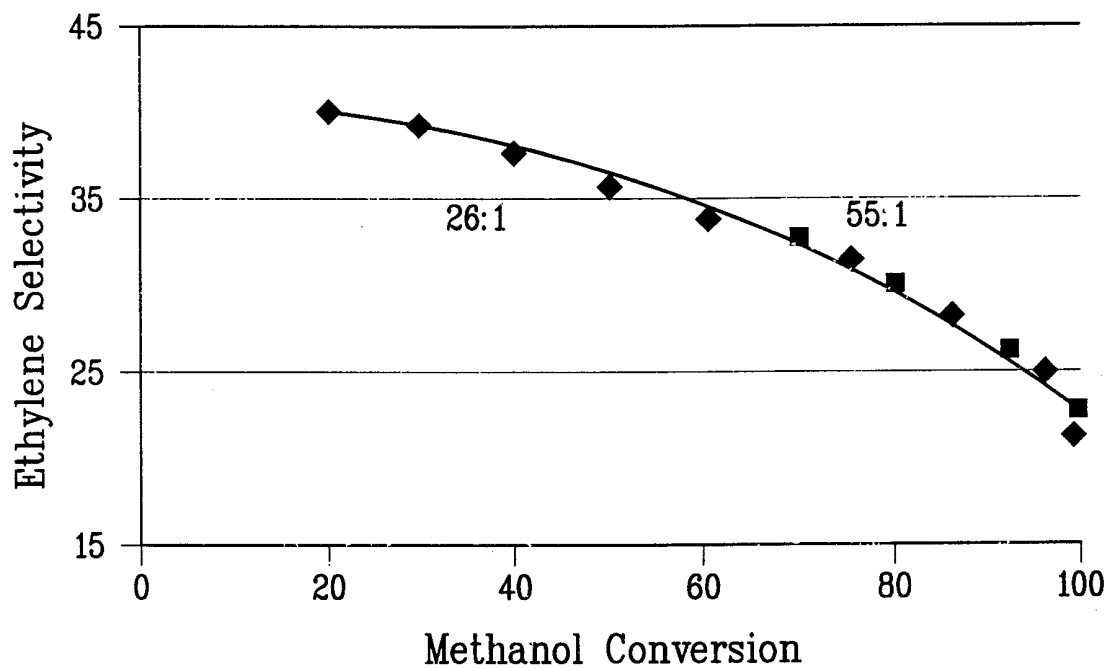


FIG. 6

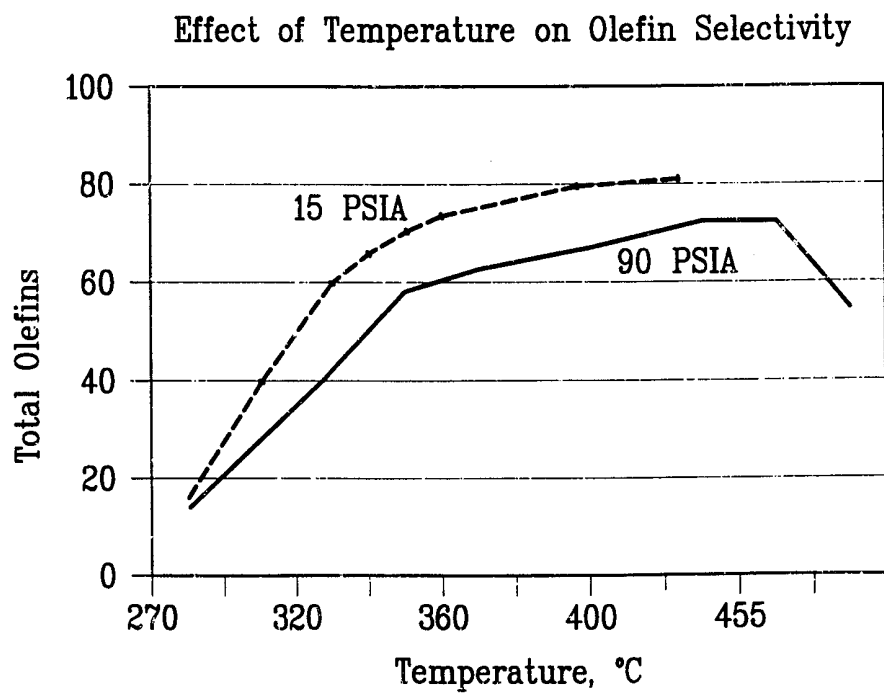
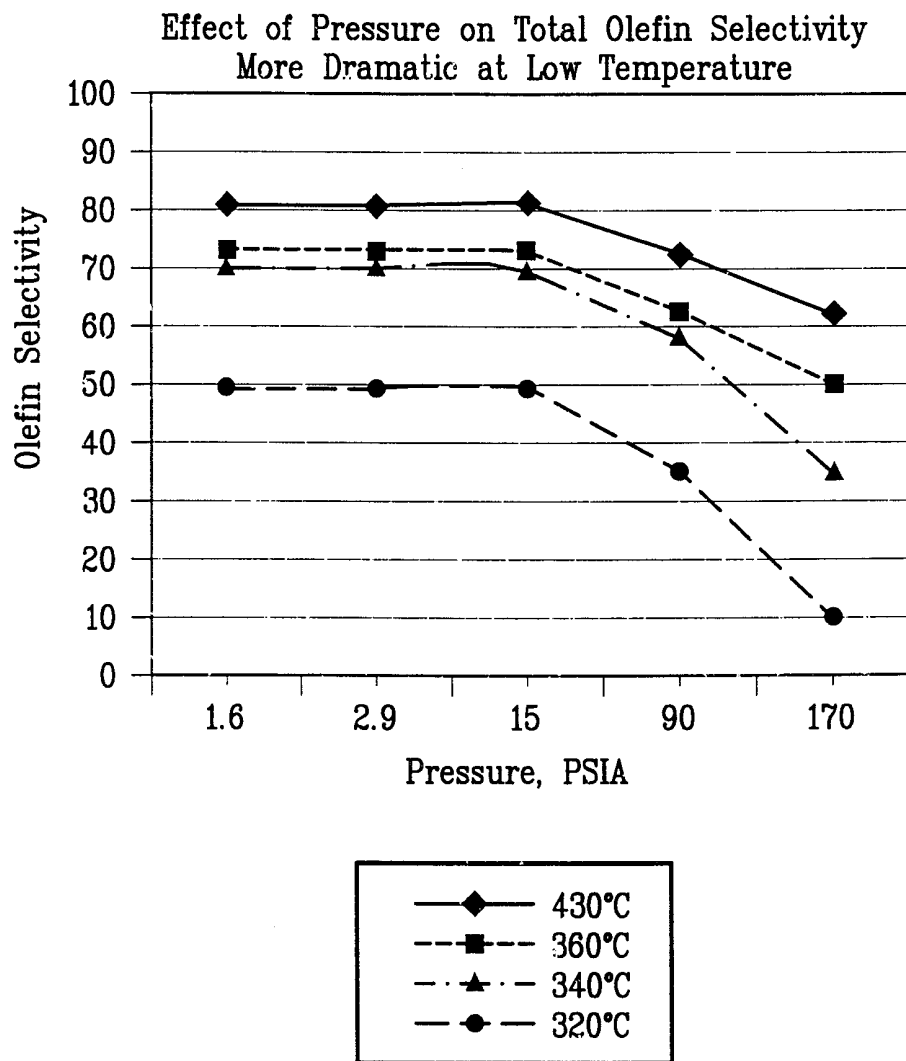
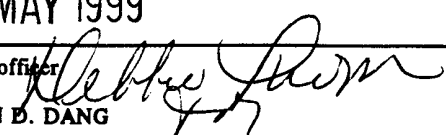


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/07311

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(6) :C07C 1/00 US CL :585/639, 640 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. : 585/639, 640		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,278,345 (JANSSEN et al) 11 January 1994 the abstract, col. 1, lines 52-65, col. 4, lines 27-40.	1-10
Y	EP 123,449 A1 (CHANG et al) 31 October 1984, the abstract.	8 and 10
Y	US 4,499,314 A (SEDDON et al) 12 February 1985, the abstract, col. 2, lines 1-11, col. 3, lines 1-43.	1-10
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier document published on or after the international filing date "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) "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	"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 "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 "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 "A" document member of the same patent family	
Date of the actual completion of the international search 07 MAY 1999		Date of mailing of the international search report 25 MAY 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3599		Authorized officer  THUAN B. DANG Telephone No. (703) 308-0661