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(54) Title: PROCESS FOR THE ALKYLATION OF BENZENE-RICH REFORMATE USING MCM-49

(57) Abrégé/Abstract:
The present invention relates to a process for alkylating a reformate feedstream containing benzene, toluene, xylenes, and ethylbenzene, said process comprising: 1) contacting said reformate feedstream with a hydrocarbon stream comprising C_2-C_5 olefins in the presence of a catalyst comprising an active form of synthetic porous crystalline MCM-49 under benzene alkylation conditions whereby an effluent stream is produced having a benzene content at least 50 wt.% less than that of said feedstream, an octane rating no less than that of said feedstream, and a total liquid product greater than that of said feedstream; and 2) collecting the gasoline boiling range fraction of said effluent stream.

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The present invention relates to a process for alkylating a reformate feedstream containing benzene, toluene, xylenes, and ethylbenzene, said process comprising: 1) contacting said reformate feedstream with a hydrocarbon stream comprising C_2-C_5 olefins in the presence of a catalyst comprising an active form of synthetic porous crystalline MCM-49 under benzene alkylation conditions whereby an effluent stream is produced having a benzene content at least 50 wt.% less than that of said feedstream, an octane rating no less than that of said feedstream, and a total liquid product greater than that of said feedstream; and 2) collecting the gasoline boiling range fraction of said effluent stream.

PROCESS FOR THE ALKYLATION OF BENZENE-RICH REFORMATE USING MCM-49

Generally, the present invention relates to a process for the production of a more environmentally suitable gasoline by removing a substantial portion of benzene in gasoline by alkylation of reformate. More particularly, the invention relates to a method to improve the conversion of benzene relative to other aromatics in gasoline feedstreams by carrying out the alkylation process using a light olefin feed at low temperature over large pore zeolite catalyst, MCM-49.

The present invention relates to a process for alkylating a benzene-containing feedstream, said process comprising:

contacting said feedstream with a hydrocarbon stream comprising C_2-C_5 olefins in the presence of a catalyst comprising an active form of synthetic porous crystalline MCM-49 under sufficient reaction conditions whereby an effluent stream is produced containing an alkylated benzene product.

In a particularly preferred embodiment, there is provided a process for alkylating a reformate feedstream containing benzene, toluene, xylenes, and ethylbenzene, said process comprising:

contacting a full-range reformate feedstream with a hydrocarbon stream comprising gaseous-phase C_2-C_5 olefins in the presence of a catalyst comprising an active form of

synthetic porous crystalline MCM-49 under at least partial liquid phase benzene alkylation conditions comprising a temperature of 150 to 350°C, a pressure of 450 to 7000 kPa, a benzene olefin molar ratio of 0.1 to 0.9, an aromatics to olefin molar ratio of 0.1 to 10, and feed WHSV of between 0.1 hr^{-1} and 500 hr^{-1}, and whereby an effluent stream is produced having a benzene content of at least 50 wt% less than that of said feedstream, an octane rating no less than that of said feedstream, and a total liquid product greater than that of said feedstream; and

collecting the gasoline boiling range fraction of said effluent stream.

The process may enhance octane number (RON) by at least 0.5.

Figure 1 depicts % conversion for benzene, toluene, ethylbenzene/xylenes, and C9 aromatics (excluding cumene) observed for alkylation of a full range reformate with propylene over MCM-49 in accordance with the present invention.

Figure 2 depicts changes in reformate octane numbers (Delta RON and MON) after alkylation of a full range reformate with propylene over MCM-49 in accordance with the present invention.

Reformates are suited to use for gasoline blending owing to their high octane number attributable to their high aromatics content. However, high concentrations of benzene in reformate, e.g., 4 to 6 wt%, can limit reformate utility

as a blending component where environmental considerations require low benzene levels in gasoline product (no greater than 1 vol%). Various efforts to reduce benzene content in reformate, e.g., selective hydrogenation, high temperature fluid-bed MBR, and reformate alkylation with methanol all suffer from octane losses or total liquid product losses associated with

undesired cracking of C5+ non-aromatics.

The present invention relates to a process whereby benzene-containing reformates are treated to reduce benzene content by alkylation while minimizing undesirable alkylation of higher boiling aromatics such as xylenes.

The catalyst employed in the present invention, MCM-49 is further described in U.S. Pat. No. 5,236,575, and U.S. Pat. No. 5,371,310.

Examples of suitable alkylating agents for use in the present invention are olefins such as ethylene, propylene, the butenes, and the pentenes. Mixtures of light olefins are especially useful as alkylating agents in the alkylation process of this invention. Accordingly, mixtures of ethylene, propylene, butenes, and/or pentenes which are major constituents of a variety of refinery streams, e.g., fuel gas, gas plant off-gas containing ethylene, propylene, etc., naphtha cracker off-gas containing light olefins, refinery FCC propane/propylene streams, and FCC off-gas, etc., are useful alkylating agents herein. For example, a typical FCC light olefin stream possesses the following composition:

	Wt.%	Mole %
Ethane	3.3	5.1
Ethylene	0.7	1.2
Propane	14.5	15.3
Propylene	42.5	46.8
Isobutane	12.9	10.3
n-Butane	3.3	2.6
Butenes	22.1	18.32
Pentanes	0.7	0.4

The term "aromatic" in reference to the alkylatable compounds which are useful herein is to be understood in accordance with its art-recognized scope which includes alkyl substituted and unsubstituted mono- and polynuclear compounds. Compounds of an aromatic character which possess a hetero atom are also useful provided they do not

act as catalyst poisons under the reaction conditions selected.

Substituted aromatic compounds which can be alkylated herein must possess at least one hydrogen atom directly bonded to the aromatic nucleus. The aromatic rings can be substituted with one or more alkyl, aryl, alkaryl, alkoxy, aryloxy, cycloalkyl, halide, and/or other groups which do not interfere with the alkylation reaction.

Suitable aromatic hydrocarbons include benzene, naphthalene, anthracene, naphthacene, perylene, coronene, and phenanthrene.

Generally the alkyl groups which can be present as substituents on the aromatic compound contain from 1 to about 22 carbon atoms and usually from about 1 to 8 carbon atoms, and most usually from about 1 to 4 carbon atoms.

Suitable alkyl substituted aromatic compounds include toluene, xylene, isopropylbenzene, normal propylbenzene, alpha-methylnaphthalene, ethylbenzene, cumene, mesitylene, durene, p-cymene, butylbenzene, pseudocumene, o-diethylbenzene, m-diethylbenzene, p-diethylbenzene, isoamylbenzene, isohexylbenzene, pentaethylbenzene, pentamethylbenzene; 1,2,3,4- tetraethylbenzene; 1,2,3,5-tetramethylbenzene; 1,2,4-triethylbenzene; 1,2,3-trimethylbenzene, m-butyltoluene; p-butyltoluene; 3,5-diethyltoluene; o-ethyltoluene; p-ethyltoluene; m-propyltoluene; 4-ethyl-m-xylene; dimethylnaphthalenes; ethylnaphthalene; 2,3-dimethylanthracene; 9-ethylanthracene; 2-methylanthracene; o-methylanthracene; 9,10-dimethylphenanthrene; and 3-methyl-phenanthrene.

Higher molecular weight alkylaromatic hydrocarbons can also be used as starting materials and include aromatic hydrocarbons such as are produced by the alkylation of aromatic hydrocarbons with olefin oligomers. Such product is frequently referred to in the art as alkylate and can include hexylbenzene, nonylbenzene, dodecylbenzene,

pentadecylbenzene, hexyltoluene, nonyltoluene, dodecyltoluene, pentadecytoluene, etc.

Reformate containing substantial quantities of benzene, toluene and/or xylene constitutes a particularly useful feed for the alkylation process of this invention. Such reformates include light reformate (C5 to 121°C (250°F)) or full range reformate (C5 to 232°C (450°F)). The present invention is especially useful in treating full range reformates which can contain mono alkylaromatics or polyalkylaromatics which are ordinarily more readily alkylatable than benzene. The present invention selectively converts benzene to alkylbenzene while maintaining relatively low alkylaromatics or polyalkylaromatics conversion. Reaction products present in the product which may be obtained from the process of the invention include ethylbenzene from the reaction of benzene with ethylene, cumene from the reaction of benzene with propylene, ethyltoluene from the reaction of toluene with ethylene, and cymenes from the reaction of toluene with propylene.

The crystalline material MCM-49 for use as catalyst component in this invention may have a composition involving the molar relationship:

$$X_2O_3:(n)YO_2,$$

wherein X is a trivalent element, such as aluminum, boron, iron, and/or gallium, preferably aluminum; Y is a tetravalent element such as silicon, titanium, and/or germanium, preferably silicon; and n is less than 35, e.g., from 2 to less than 35, usually from 10 to less than 35, more usually from 15 to 31. In the as-synthesized form, the material may have a formula, on an anhydrous basis and in terms of moles of oxides per n moles of YO_2, as follows:

$$(0.1-0.6)M_2O:(1-4)R:X_2O_3:nYO_2$$

wherein M is an alkali or alkaline earth metal, and R is an organic moiety. The M and R components are associated with the material as a result of their presence during

crystallization, and are easily removed by post-crystallization methods hereinafter more particularly described.

MCM-49 is thermally stable and in the calcined form exhibits high surface area (greater than 400 m^2/gm) and unusually large sorption capacity when compared to previously described materials such as calcined PSH-3 and SSZ-25 having similar X-ray diffraction patterns. To the extent desired, the original sodium cations of the as-synthesized material can be replaced in accordance with techniques well known in the art, at least in part, by ion exchange with other cations. Preferred replacing cations include metal ions, hydrogen ions, hydrogen precursor, e.g., ammonium, ions, and mixtures thereof. Particularly preferred cations are those which tailor the catalytic activity for certain hydrocarbon conversion reactions. These include hydrogen, rare earth metals, and metals of Groups IIA, IIIA, IVA, IB, IIB, IIIB, IVB and VIII of the Periodic Table of the Elements.

The catalyst described herein can also be used in intimate combination with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such component can be introduced in the catalyst composition by way of co-crystallization, exchanged into the composition to the extent a Group IIIA element, e.g., aluminum, is in the structure, impregnated therein or intimately physically admixed therewith. Such component can be impregnated in, or on, the zeolite such as, for example, by, in the case of platinum, treating the zeolite with a solution containing a platinum metal-containing ion. Thus, suitable platinum compounds for this purpose include chloroplatinic acid, platinum halides, and various compounds containing the platinum ammine complex. The presence of a hydrogenation component in the catalyst

can facilitate its hydrogenative regeneration.

Zeolite MCM-49, especially in its metal, hydrogen and ammonium forms, can be beneficially converted to another form by thermal treatment. This thermal treatment is generally performed by heating one of these forms at a temperature of at least about 370°C for at least 1 minute and generally not longer than 20 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is preferred simply for reasons of convenience. The thermal treatment can be performed at a temperature of up to about 925°C.

Prior to its use in a catalytic process, the zeolite MCM-49 crystals may be dehydrated, at least partially. This can be done by heating the crystals to a temperature in the range of from about 200°C to about 595°C in an atmosphere such as air, nitrogen, etc., and at atmospheric, subatmospheric or superatmospheric pressures for between about 30 minutes to about 48 hours. Dehydration can also be performed at room temperature merely by placing the crystalline material in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

It may be desired to incorporate the MCM-49 with another material resistant to the temperatures and other conditions employed in organic conversion processes. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica, silica-alumina, and/or metal oxides such as alumina, TiO_2, or ZrO_2. 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 in conjunction with the new crystal, i.e., combined therewith or present during synthesis of the new crystal, which is active, tends to change the conversion and/or selectivity of the catalyst in certain organic conversion processes. Inactive materials 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 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 new crystal 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. Binders useful for compositing with the present crystal also include inorganic oxides, notably alumina, as well as titania or zirconia.

In addition to the foregoing materials, MCM-49 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.

The relative proportions of finely divided crystalline material and inorganic oxide matrix vary widely, with the crystal 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 stability of zeolite MCM-49 may be increased by combining the as-synthesized MCM-49 with an alumina binder, converting the alumina-bound MCM-49 to the hydrogen form, (i.e., HMCM-49) and steaming the alumina-bound HMCM-49 composition under conditions sufficient to increase the stability of the catalyst. U.S. Patent Nos. 4,663,492; 4,594,146; 4,522,929; and 4,429,176 describe conditions for the steam stabilization of zeolite catalysts which can be utilized to steam-stabilize alumina-bound HMCM-49. The steam stabilization conditions include contacting the alumina bound HMCM-49 with, e.g., 5-100% steam at a temperature of at least about 300°C (e.g., 300-650°C) for at least one hour (e.g., 1-200 hours) at a pressure of 101-2,500 kPa. In a more particular embodiment, the catalyst can be made to undergo steaming with 75-100% steam at 315°-500°C and atmospheric pressure for 2-25 hours. In accordance with the steam stabilization treatment described in the above-mentioned patents, the steaming of the catalyst can take place under conditions sufficient to initially increase the Alpha Value of the catalyst, the significance of which is discussed infra, and produce a steamed catalyst having a peak Alpha Value. If desired, steaming can be continued to subsequently reduce the Alpha Value from the peak Alpha Value to an Alpha Value which is substantially the same as or less than the Alpha Value of the unsteamed catalyst.

The alkylation process of this invention is conducted such that the organic reactants, i.e., the alkylatable aromatic compound and the alkylating agent, are brought into contact with the zeolite MCM-49 catalyst composition in a suitable reaction zone such as, for example, in a flow reactor containing a fixed bed of the catalyst composition, under effective alkylation conditions. Such conditions

include a temperature of from 0°C to 500°C, and preferably between 50°C and 250°C. The reaction generally takes place at pressures of from 20 to 25,500 kPa (0.2 to 250 atmospheres) and preferably from 1 to 25 atmospheres. The molar ratio of alkylatable aromatic compound to alkylating agent can be from 0.1:1 to 50:1 and preferably can be from 0.5:1 to about 5:1. Reaction is suitably accomplished utilizing a feed weight hourly space velocity (WHSV) of between 0.1 hr^{-1} and 500 hr^{-1} and preferably from 0.5 hr^{-1} to 100 hr^{-1}. The latter WHSV is based upon the total weight of active catalyst (and binder if present).

The reactants can be in either the vapor phase or the liquid phase and can be neat, i.e., free from intentional admixture or dilution with other material, or they can be brought into contact with the zeolite catalyst composition with the aid of carrier gases or diluents such as, for example, hydrogen or nitrogen.

The alkylation process described herein can be carried out as a batch-type, semi-continuous or continuous operation utilizing a fixed or moving bed catalyst system. A particular embodiment entails use of a catalyst zone wherein the hydrocarbon charge is passed concurrently or countercurrently through a moving bed of particle-form catalyst. The latter, after use, is conducted to a regeneration zone where coke is burned from the catalyst in an oxygen-containing atmosphere (such as air) at elevated temperature, after which the regenerated catalyst is recycled to the conversion zone for further contact with the organic reactants.

When benzene is alkylated with ethylene to produce ethylbenzene, the alkylation reaction may be carried out in the liquid phase. Suitable liquid phase conditions can be selected by reference to the phase diagram for benzene. In the liquid phase, the reaction is carried out with the benzene feedstock in the liquid phase with the reaction conditions (temperature, pressure) appropriate to this end.

Liquid phase operation may be carried out at temperatures between 300° and 500°F (150° to 260°C), usually in the range of 400° to 500°F (205° to 260°C). Pressures during the liquid phase alkylation step may be as high as 3000 psig, (20875 kPa abs.) and generally will not exceed 1000 psig (7000 kPa). The reaction may be carried out in the absence of hydrogen and accordingly the prevailing pressures are those of the reactant species. In a high pressure liquid phase operation, the temperature may be from 150 to 290°C (300° to 552°F) (benzene's critical temperature) with the pressure in the range of 2860 to 5620 kPa (400 to 800 psig). The space velocity may be from about 0.1 to 10 WHSV, based on the ethylene feed, although lower space velocities are preferred for the liquid phase reaction, for example, from 0.1 to 1 WHSV with values from 0.2 to 0.5 WHSV (ethylene) being typical.

When benzene is alkylated with propylene to produce cumene, the reaction may also take place under liquid phase conditions including a temperature of up to 150°C, e.g., from 10°C to 125°C, a pressure of from 1 to 30 atmospheres, and an aromatic hydrocarbon weight hourly space velocity (WHSV) of from 5 hr^{-1} to 50 hr^{-1}.

When conducting alkylation according to the process of this invention, various types of reactors can be used. For example, the process can be carried out in batchwise fashion by adding the catalyst and aromatic feedstock to a stirred autoclave, heating to reaction temperature, and then slowly adding the olefinic or polyalkylaromatic feedstock. A heat transfer fluid can be circulated through the jacket of the autoclave, or a condenser can be provided, to remove the heat of reaction and maintain a constant temperature. Large scale industrial processes may employ a fixed-bed reactor operating in an upflow or downflow mode or a moving-bed reactor operating with concurrent or countercurrent catalyst and hydrocarbon flows. These reactors may contain a single catalyst bed or

multiple beds and may be equipped for the interstage addition of olefins and interstage cooling. Interstage olefin addition and more nearly isothermal operation enhance product quality and catalyst life. A moving-bed reactor makes possible the continuous removal of spent catalyst for regeneration and replacement by fresh or regenerated catalysts. The present invention may also be carried out using an ebullated bed reactor or slurry reactor.

In a fixed-bed reactor or moving-bed reactor, alkylation is completed in a relatively short reaction zone following the introduction of olefin.

In order to more fully illustrate the nature of the invention and the manner of practicing same, the following examples are presented.

EXAMPLE 1

1.0 grams (2.0 cc, sized to 0.16 cm x 0.16 cm (1/16" x 1/16") of MCM-49 catalyst (containing 35 wt% alumina binder and having an alpha value of 910) was mixed with 10 cc of 20-40 mesh Vycor™ chips, and then charged into an isothermal tubular reactor. The catalyst was dried at 101 kPa (1 atm.) with 50 cc/min of N_2 for four hours. The reactor temperature was then adjusted to 129°C and the reactor pressure was increased to 2170 kPa (300 psig) before a full range reformate was fed into the reactor at a WHSV of 17. The full range reformate, obtained from a CCR pilot unit (Continuous Catalytic Reforming), contained 5.475 wt% benzene and had a specific gravity of 0.8075, a research octane number (R+O) of 100.62, and a motor octane number (M+O) of 90.90. The N_2 gas was then cut off. After the catalyst was wetted with the reformated feed, propylene was fed into the reactor at a WHSV of 0.5. The volume of effluent gas was measured by wet test meter. After the system was lined out, a four hour material balance was made, and the results showed that propylene conversion was 81.14%, benzene conversion was 8.51%, liquid yield was

103.31 wt% (102.86 vol%), and the octane number of the liquid product was reduced slightly (delta RON = -0.2, delta MON = -0.7). estimated to be mostly unchanged.

EXAMPLE 2

The alkylation process of Example 1 was continued with all operating conditions remaining the same except that the reaction temperature was raised to 154°C and propylene was fed into the reactor at a WHSV of 2.26. The results showed that propylene conversion was 96.63 wt%, benzene conversion was 58.20 wt%, liquid yield was 113.29 wt% (112.39 vol%). Delta RON was 0, and delta MON was -0.7.

EXAMPLE 3

The alkylation process of Example 2 was continued with all operating conditions remaining the same except that propylene was fed into the reactor at a WHSV of 2.76. The results showed that propylene conversion was 96.1 wt%, benzene conversion was 68.5 wt%, liquid yield was 116.2 wt% (115.17 vol%). Delta RON was 0, and delta MON was -0.2.

EXAMPLES 4 TO 8

The alkylation process of Example 2 was continued with all operating conditions remaining the same except that the feed set out in Table III containing 4.573 wt% benzene was used, temperature was varied from 154°C to 348°C, propylene was fed into the reactor at a WHSV of 2.0, reformate WHSV was varied from 16.6 to 17.1, propylene to benzene molar ratio ranged from 4.8 to 4.9. The results, set out in Table III below showed high propylene conversion (97.26 to 99.87 wt%), high benzene conversion (57.11 wt% to 70.21 wt%).

Benzene conversion was shown to improve when alkylation is carried out at temperatures ranging from 225 to 300°C. Figure 1 shows the % conversion for benzene, toluene, EB/xylenes, and C9 aromatics (excluding cumene which is the major alkylation product derived from benzene). Suppressing the conversion of the existing alkylaromatics in the feed is desirable inasmuch as they

are already desirable components of reformate requiring no further alkylation. Maximizing benzene conversion is desirable in order to meet product specifications for low benzene content. The conversion of reformate benzene to cumene by alkylation provides a suitable way to remove benzene while improving liquid yield without adversely affecting octane number.

Figure 2 depicts the effect on octane numbers (RON, MON) for the reformate of Examples 4 to 8 treated in accordance with the present invention. A net increase for both RON and MON was observed at temperatures over 185°C.

TABLE III

Liquid Phase Reformate/C3= Alkylation Over MCM 49/35% Al203 at 2170 kPa (300 psig)

	Feed	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
TOS, days		25.6	26.6	29.4	30.5	32.6
Temperature, °C		154.0	198.0	248.0	298.0	348.0
C3-WHSV		2.00	2.00	2.00	2.00	2.00
Reformate WHSV		16.6	16.9	17.0	17.0	17.1
C3-/Bz molar ratio		4.9	4.8	4.8	4.8	4.8
Total material balance		100.8	100.7	100.5	100.0	101.1
Conversion, wt.%						
C3=		99.87	99.80	97.45	97.26	98.01
Benzene		57.11	59.69	70.21	65.02	56.68
Toluene		47.18	48.22	50.99	44.77	38.83
EB + Xylenes		30.79	30.89	28.55	24.88	20.20
C9 Ar (minus cumene)		18.26	17.23	14.02	12.97	7.97
Product Wt% Distribution						
C1	0.000	0.000	0.000	0.000	0.000	0.000
C2=	0.000	0.000	0.000	0.000	0.000	0.000
C2	0.006	0.006	0.006	0.006	0.006	0.009
C3=/C3	0.182	0.386	0.253	0.302	0.648	1.613
I-C4	0.381	0.367	0.373	0.503	0.709	0.705
i-C4=/1-C4=	0.007	0.000	0.000	0.000	0.000	0.044
n-C4	0.618	0.591	0.580	0.616	0.601	0.598
t-C4=	0.000	0.000	0.000	0.000	0.000	0.023
c-C4=	0.000	0.000	0.000	0.000	0.000	0.000
1-C5	1.344	1.281	1.272	1.439	1.472	1.396
1-C5=	0.000	0.000	0.000	0.000	0.000	0.000

2-M-1-C4=	0.000	0.000	0.000	0.000	0.000	0.000
n-C5	0.995	0.934	0.917	0.970	0.929	0.903
t-2-C5=	0.009	0.008	0.000	0.000	0.000	0.013
c-2-C5=/2-M-2-C4=	0.005	0.000	0.000	0.000	0.000	0.056
2,2-BM-C4	0.542	0.511	0.502	0.527	0.519	0.490
c-C5=/4-M-1-C5=	0.018	0.000	0.000	0.000	0.000	0.010
c-C5/2,3-DM-C4	0.781	0.737	0.731	0.795	0.822	0.834
2-M-C5	2.441	2.318	2.280	2.425	2.378	2.258
3-M-C5	1.895	1.790	1.779	1.896	1.852	1.762
2-M-1-C5=	0.031	0.013	0.000	0.000	0.000	0.032
n-C6	2.369	2.216	2.174	2.279	2.198	2.121
C6=,Σ	0.125	0.099	0.005	0.000	0.000	0.147
M-c-C5	0.286	0.270	0.252	0.219	0.207	0.242
C7P (others),Σ	3.963	3.561	3.465	3.602	3.429	3.569
Bz	4.573	1.737	1.636	1.215	1.436	1.758
c-C6	0.000	0.000	0.000	0.000	0.000	0.000
n-C7	1.049	0.972	0.939	0.978	0.952	0.926
Tol	15.100	7.063	6.940	6.603	7.485	8.197
C8P (others),Σ	1.149	1.101	1.095	1.083	1.122	1.027
n-C8	0.333	0.305	0.301	0.298	0.296	0.301
EB	3.798	2.775	2.660	2.383	1.993	2.461
m-, p-Xyl	13.549	9.151	9.171	9.902	10.438	10.763
o-Xyl	5.696	2.195	2.306	2.405	3.105	3.092
C9P (others),Σ	0.620	0.803	0.536	0.447	0.412	0.424
n-C9	0.127	0.134	0.129	0.117	0.109	0.116
Cumene	0.457	3.743	3.542	3.814	3.346	3.185
n-C3-Bz	1.571	1.211	1.181	1.089	0.916	1.157
m-, p-Et-Tol	6.872	5.465	5.467	5.442	5.474	5.795
1,3,5-TMB	2.165	1.898	1.928	1.951	2.082	2.008
o-Et-Tol	1.775	1.258	1.239	1.130	0.889	1.130
1,2,4-TMB	7.526	4.858	5.082	5.912	6.428	6.415
i-C4-Bz/sec-C4-Bz	0.349	0.284	0.287	0.265	0.163	0.255

1,2,3-TMB (est.)	1.012	0.653	0.684	0.795	0.865	0.863
m-Cymene (est.)	0.895	2.055	2.354	4.852	5.500	4.077
p-, o-Cymene	0.125	7.695	7.048	5.003	3.110	3.460
indane	0.568	0.212	0.208	0.167	0.130	0.181
Other C10 Ar,Σ	10.088	9.428	9.864	10.771	12.695	11.092
Naphthalene	0.947	0.436	0.459	0.359	0.263	0.272
C11-C12 Ar, Σ	2.032	16.292	16.544	14.048	11.351	10.614
2-M-Naph	0.701	0.459	0.515	0.405	0.319	0.356
1-M-Naph	0.355	0.271	0.283	0.247	0.137	0.183
DM-Naph, Σ	0.355	1.771	1.995	1.643	1.345	1.595
C13+	0.211	0.685	1.019	1.098	1.869	1.471
Σ	100.000	100.000	100.000	100.000	100.000	100.000

WHAT IS CLAIMED IS:

1. A process for alkylating a reformate feedstream containing benzene, toluene, xylenes, and ethylbenzene, said process comprising:

contacting a full-range reformate feedstream with a hydrocarbon stream comprising gaseous-phase C_2-C_5 olefins in the presence of a catalyst comprising an active form of synthetic porous crystalline MCM-49 under at least partial liquid phase benzene alkylation conditions comprising a temperature of 150 to 350°C, a pressure of 450 to 7000 kPa, a benzene olefin molar ratio of 0.1 to 0.9, an aromatics to olefin molar ratio of 0.1 to 10, and feed WHSV of between 0.1 hr^{-1} and 500 hr^{-1}, and whereby an effluent stream is produced having a benzene content at least 50 wt% less than that of said feedstream, an octane rating no less than that of said feedstream, and a total liquid product greater than that of said feedstream; and

collecting the gasoline boiling range fraction of said effluent stream.

2. The process of claim 1 wherein said hydrocarbon stream comprising C_2-C_5 olefins contains at least 30 wt% propylene and said benzene alkylation conditions comprise temperature between 200 and 300°C, pressure between 790 and 3550 kPa, and weight hourly space velocity between 0.5 hr^{-1} to about 100 hr^{-1}.

3. The process of claim 2 wherein said hydrocarbon stream comprising C_2-C_5 olefins contains at least 40 wt% propylene and said reformate feedstream is a full range reformate (C5 to 232°C).

4. The process of any one of claims 1 to 3 wherein said catalyst is present in the form of a fixed-bed.

5. The process of any one of claims 1 to 4 wherein said synthetic porous crystalline MCM-49 has been treated to replace original cations, at least in part, with a cation or mixture of cations selected from the group consisting of hydrogen, hydrogen precursors, rare earth metals, and metals of Groups IIA, IIIA, IVA, IB, IIB, IIIB, IVB, VIB and VIII of the Periodic Table.

6. The process of any one of claims 1 to 5 which further comprises blending said gasoline boiling range fraction with a non-reformate gasoline boiling range fraction to provide a gasoline boiling range product containing no greater than 1 vol% benzene.

7. A process according to any one of claims 1 to 6 wherein said gasoline boiling range fraction has an octane number (RON) at least 0.5 greater than that of said reformate.

8. A process according to any one of claims 1 to 7 wherein said hydrocarbon stream is a refining FCC propane/propylene stream, and said liquid product contains cumene.

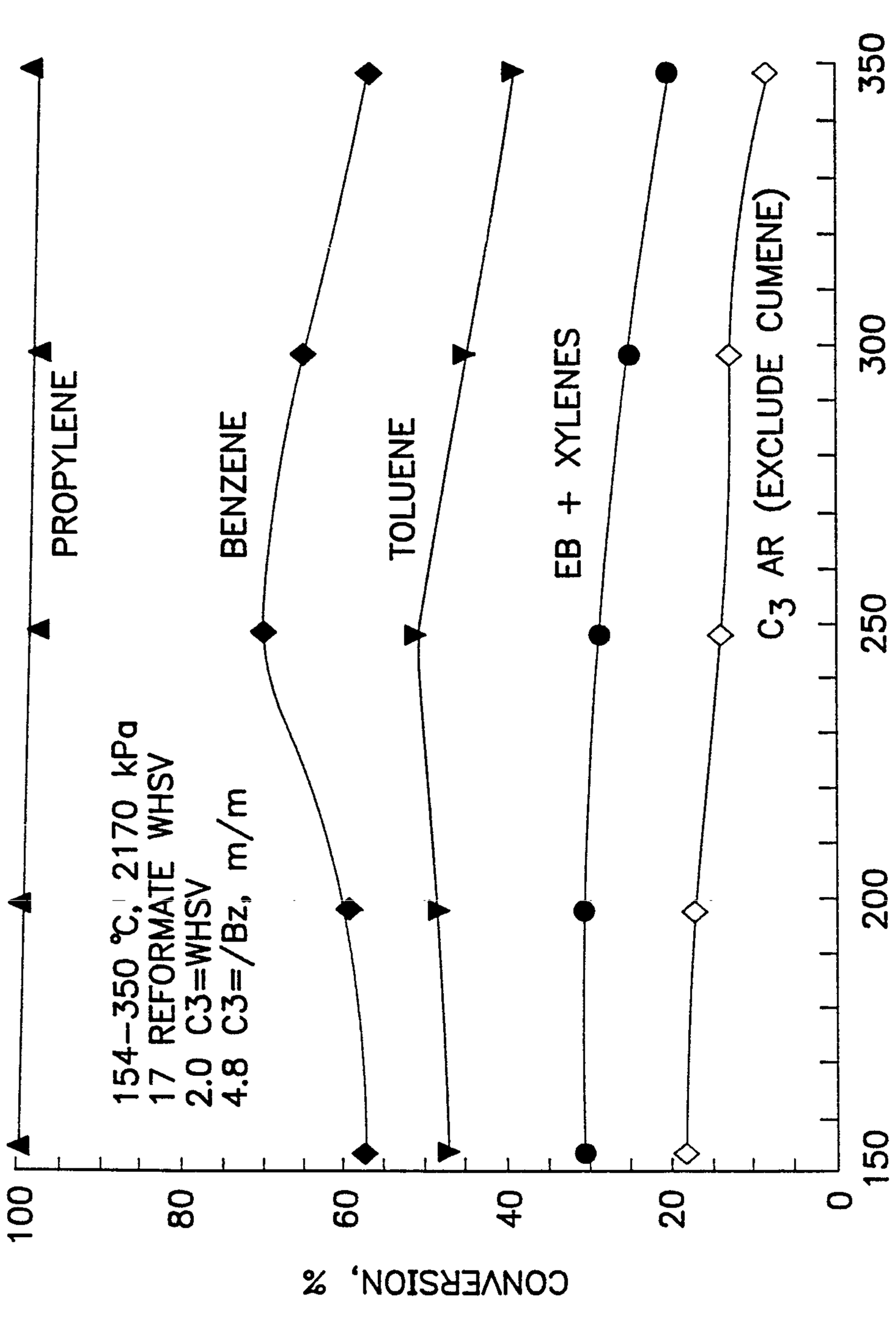
PROPYLENE
BENZENE
TOLUENE
EB + XYLENES
C3 AR (EXCLUDE CUMENE)
154–350 °C, 2170 kPa
17 REFORMATE WHSV
2.0 C3=WHSV
4.8 C3=/Bz, m/m
100
80
60
40
20
0
150
200
250
300
350
CONVERSION, %
TEMPERATURE, °C

FIG. 1

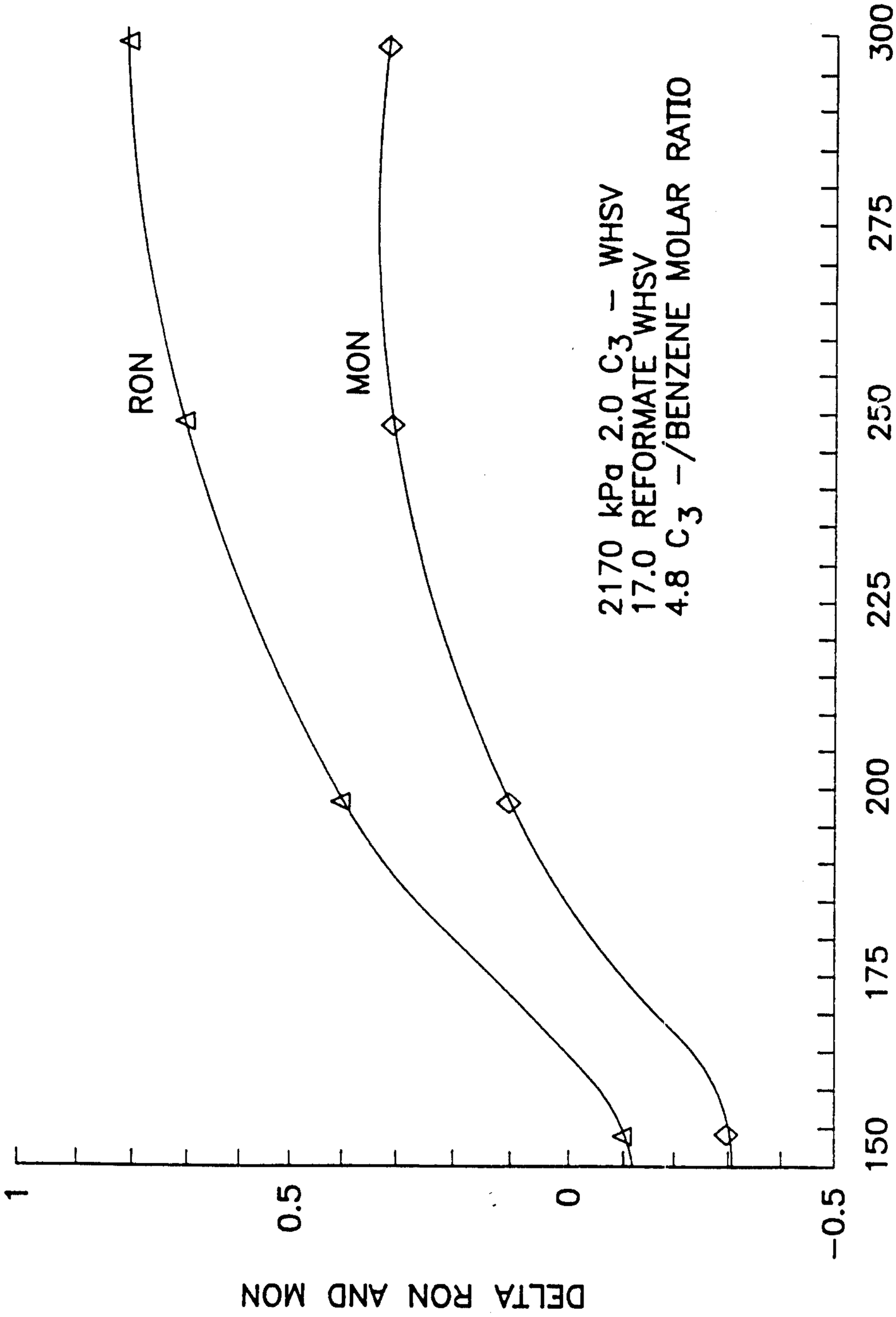
RON
MON
2170 kPa 2.0 C3 – WHSV
17.0 REFORMATE WHSV
4.8 C3 –/BENZENE MOLAR RATIO
175
200
225
250
275
300
TEMPERATURE, °C
150
1
0.5
0
-0.5
DELTA RON AND MON

FIG. 2