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Catalytic Cracking of a Hydrocarbon Mixture on Combinations of HY and HZSM-5 Zeolites

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Catalytic cracking of a hydrocarbon mixture has been examined on HY and HZSM-5, using both individual catalysts and a combination of these zeolites. Product distributions obtained from cracking on the faujasite alone have been compared with those on the zeolite combination. Product distributions have been calculated for reactions on the catalyst combinations by assuming relative contributions based on the individual product distributions as well as the conversions on the individual components. A comparison of product distributions for cracking on the faujasite with that on the faujasite–pentasil combination shows that the ZSM-5 additive inhibits secondary reaction processes, particularly hydrogen transfer occurring on the faujasite. The olefins produced on the faujasite are further cracked on the pentasil additive, leading to increased yields of C_3 and C_4 olefins. Shifts in branched-to-linear ratios for both paraffins and olefins may be attributed to isomerisation processes occurring on the ZSM-5. Calculated distributions provide a reasonable approximation to those observed, with variances in the product yields providing further evidence for reduced hydrogen transfer on zeolite combinations.

INTRODUCTION

Numerous studies of gas-oil cracking over a Y-based catalyst with a small amount (often less than 5% by weight) of ZSM-5 additive have been presented (*1–9*). Results suggest an improved gasoline octane-rating is obtained at the expense of yield. However, the mechanisms by which the ZSM-5 additive promotes octane enhancement are still under debate. Relatively few studies have reported the cracking behaviour of model hydrocarbon mixtures on combinations of zeolites.

In the present study, the behaviour of a complex hydrocarbon feedstock, consisting of normal and branched paraffins, alkylated aromatics, and alicyclics, has been investigated under cracking conditions in the presence of faujasite–pentasil combinations. The product distributions obtained for feed cracking on the individual zeolites have been compared with those obtained on a combination of the two catalysts. By noting differences between the product distribution obtained on the individual HY and HZSM-5 zeolites, and that on the zeolite mixture {Y + Z}, conclusions regarding the action of the additive may be postulated. The results obtained have also been discussed with reference to published observations for the cracking of gas-oils on such catalyst combinations.

EXPERIMENTAL

A feedstock mixture consisting of seven major hydrocarbon components (each obtained from Aldrich and used without further purification) was prepared, with a composition shown in Table 1 chosen to approximately represent a gas-oil. Other minor components due to impurities in the individual hydrocarbons are also included in Table 1 as branched C_{12} paraffins and branched C_{12} aromatics.

HY zeolite (CBV 500, Si/Al = 3.2) was provided by PQ zeolites, the Netherlands. HZSM-5 (Si/Al = 105) was provided by Snamprogetti, Milan, Italy. Details of the synthesis and characterisation of the pentasil have been reported previously (*10*). Catalysts of mesh size 80/100 were calcined at 500°C prior to use.

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TABLE 1

Composition of the Feedstock Used in This Study

Component	Mol formula	Weight (%)	Molar ratio (%)
n-Dodecane	$C_{12}H_{26}$	53.8	54.07
1-Methylnaphthalene	$C_{11}H_{10}$	15.5	18.62
2,2,4,6,6,8,8 Heptamethylnonane	$C_{16}H_{34}$	11.5	8.73
Cyclododecane	$C_{12}H_{24}$	5.0	5.02
Phenylheptane	$C_{13}H_{20}$	12.5	12.11
9-Methylanthracene	$C_{15}H_{12}$	0.4	0.33
Dodecahydrotriphenylene	$C_{18}H_{24}$	0.5	0.30
Branched C_{12} paraffins[a]	$C_{12}H_{26}$	0.4	0.40
Branched C_{12} aromatics[b]	$C_{12}H_{18}$	0.4	0.42

[a] Impurity introduced with *n*-dodecane.
[b] Impurity introduced with cyclododecane.

All experiments were performed by using an integral, fixed-bed gas-phase plug-flow reactor with independently controlled three-zone heater. The experimental apparatus and procedures used were similar to those described previously (*11*, *12*). All reactions were carried out at 400°C and 1 atm pressure. Catalysts were mixed with granules of washed sand, serving as a support matrix within the reactor. Blank experiments were performed to determine the extent of thermal cracking (less than 1% at longest times on stream). All thermal products were subtracted from yield of catalytic products.

In all experiments, 5 g of feed were injected over the catalyst at varying rates controlled by the feed-syringe pump. Two catalyst to feed ratios were used for the HY zeolite (0.0404 and 0.178). The amount of HZSM-5 used was approximately 5% by weight of the HY zeolite, giving catalyst to feed ratios of 0.002 and 0.010 for the pentasil. Experiments on zeolite combinations were undertaken by combining the corresponding masses of HY and HZSM-5.

Liquid products were analysed using a Hewlett–Packard 5890A gas chromatograph with a BP10 capillary column (25 m × 0.32 mm i.d.) and flame ionisation detector. Gaseous products were also analysed using a Hewlett–Packard gas chromatograph of the same type with a Chrompak capillary column (25 m × 0.32 mm i.d.). Data handling was facilitated using a DAPA software package. Identification of hydrocarbon products was assisted by the use of a Hewlett–Packard 5890 gas chromatograph coupled to a 5970 mass selective detector.

RESULTS AND DISCUSSION

In this study, the cracking behaviour of a complex model-feedstock at 400°C has been investigated on HY and HZSM-5 zeolites, both individually and in combination. Although the experimental conditions (fresh catalysts, 400°C) are removed from those used in industrial FCC units, the model study serves to indicate the type of reactions undergone by hydrocarbons when ZSM-5 is added to a faujasite cracking catalyst. Our experimental conditions can be contrasted with those of Madon (*8*), where high-temperature steam treatment of the individual catalyst components was used to simulate the deactivation occurring in a commercial FCC unit; temperatures in excess of 500°C were used for cracking of gas-oils. The percentage of the HZSM-5 additive (5% by weight) is comparable to the proportions used industrially in FCC units (from 0.5 to 3%) (*1*, *2*, *6*, *13–15*). Figures 1a and 1b show the feed conversion, defined as the weight percent of all products including coke, as a function of time-on-stream (TOS) for the individual catalysts and in combination under two sets of conditions. In each case, feed conversion over the base HY catalyst is increased by pentasil addition. However, the increase in conversion is less than that predicted by the simple addition of individual conversions.

In considering the effects of zeolite combinations as a cracking catalyst, two approaches may be taken. First, the influence of the additive (HZSM-5) on feedstock removal or product appearance can be considered with reference to the original distributions on the faujasite alone. This approach has been taken in reporting results for pentasil addition during cracking of gas-oils (*1–8*). Secondly, it is possible to compare the observed distributions with that calcu-

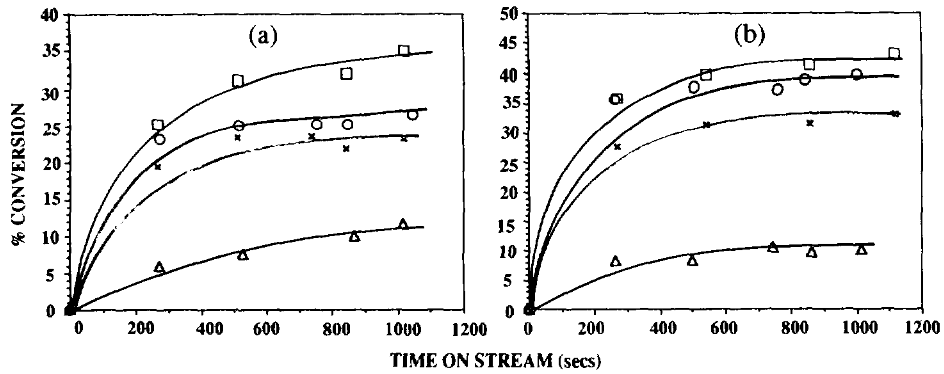

FIG. 1. Effects of time-on-stream and catalyst-to-feed ratios for feedstock conversion on HY (×), HZSM-5 (△), the faujasite/pentasil zeolite combination {Y + Z} (○), and predicted value for the combination at 400°C (□). Cat/feed ratios for reaction on: (a) HY = 0.0404; HZSM-5 = 0.0019; zeolite combination = 0.0423. (b) HY = 0.1780; HZSM-5 = 0.0090; zeolite combination = 0.1870.

lated for the combination, based on the observed behaviour on the isolated catalysts. Differences between observed and predicted distributions can be ascribed to additional processes (e.g., interactions between one catalyst and the products from the other).

Disappearance of Feedstock Components

One advantage of using a feedstock prepared by mixing a set of pure hydrocarbons is that not only is it possible to observe the appearance of product species, but also the concurrent disappearance of each individual component present in the original feedstock. This is very difficult in the case of complex gas-oils, which contain hundreds of different component species.

Figures 2a and 2b show comparisons between the distributions of feedstock components removed on the individual catalysts. The general distribution patterns were not significantly altered by time on stream, ranging from 200 to 1200 sec in these studies. On HY, reaction of *n*-dodecane and methylnaphthalene contribute over 72% of the total feedstock components removed. Reaction of cyclododecane, heptamethylnonane and phenylheptane each contribute 5 to 11%, while the combined contributions of methylanthracene and dodecahydrotriphenylene is less than 1.5%. On HZSM-5, the contribution from methylnaphthalene is reduced to less than 30% of that on HY, with the contribution from the *n*-paraffin increased to 51% of the total feedstock removed. The relative importance of the contribution from cracking of phenylheptane is also increased on HZSM-5 and accounts for 24% of the total. As on HY, cracking of methylanthracene and dodecahydrotriphenylene on HZSM-5 contributes a minor amount (<1.7%) of the total.

Figures 3a and 3b show the influence of HZSM-5 as a cracking additive by comparing observed distributions represented by {HY} and {Y + Z} under identical conditions at two different times-on-stream. Pentasil addition increases the selectivity for cracking of *n*-dodecane and phenylheptane. Previous studies (*9*, *13*, *14*) have also found HZSM-5 addition leads to increased selectivity for removal of linear paraffins from a mixed feedstock. Relative contributions from cyclododecane, methylnaphthalene, and methylanthracene cracking decrease with the pentasil present, while the selectivities for heptamethylnonane and dodecahydrotriphenylene remain essentially unchanged. Also shown in Fig. 3 is a product distribution calculated from observed distributions on the individual catalysts using rel-

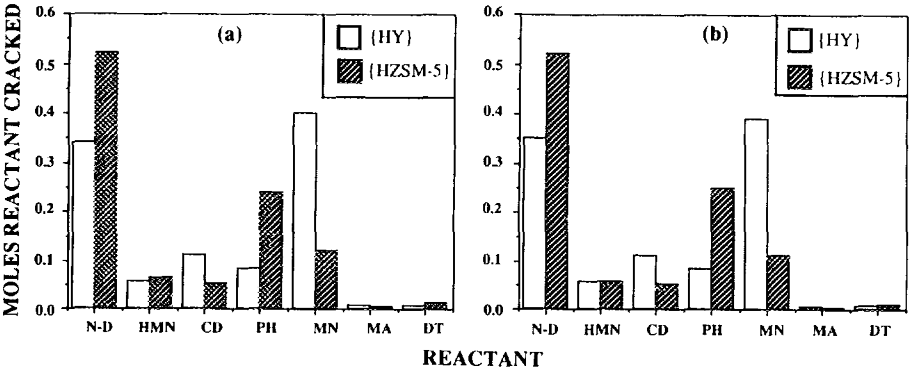

FIG. 2. Removal of feedstock components on HY and HZSM-5 at 400°C, representative examples with cat/feed ratios: HY = 0.1780, HZSM-5 = 0.0090 and time-on-stream (a) 500 sec and (b) 840 sec. Feedstock components: N-D = dodecane; HMN = heptamethylnonane; CD = cyclododecane; PH = phenylheptane; MN = methylnaphthalene; MA = methylanthracene; DT = dodecahydrotriphenylene.

ative contributions of the distributions from reaction on HY and HZSM-5, weighted according to their contribution to total conversion, as illustrated in Fig. 1. The calculated distribution has been designated {Y* + Z*}. Comparisons of the product distributions {Y + Z} and {Y* + Z*} in Fig. 3 show that the calculated distribution provides a very reasonable representation of that observed experimentally. In terms of the selectivity of feedstock component removal, as well as total conversion (Fig. 1), the effect of the two catalysts can be regarded as independent and additive to a first approximation. Inspection of Fig. 3 shows that more *n*-dodecane and phenylheptane are removed than predicted, while lower proportions of methylnaphthalene, cyclododecane, and heptamethylnonane are removed.

The distributions shown in Figs. 2 and 3 give the relative contribution of each component to the overall removal of the feedstock. This contribution will be affected by both the relative amounts of each compo-

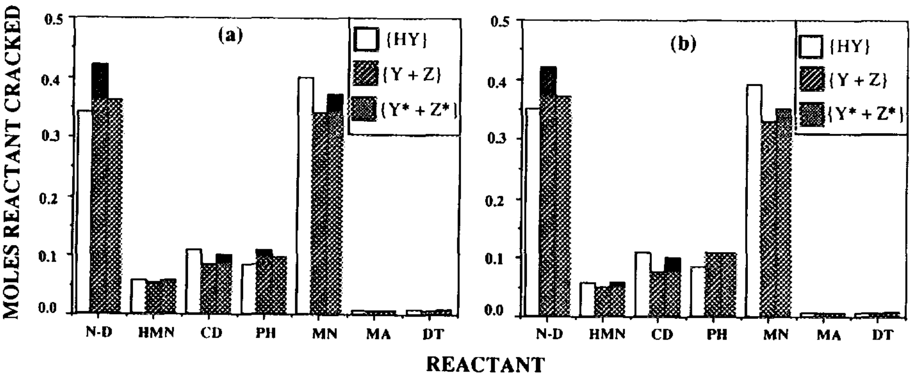

FIG. 3. Removal of feedstock components at 400°C on HY Catalyst {HY}, the faujasite/pentasil zeolite combination {Y + Z} and predicted value for the faujasite/pentasil combination {Y* + Z*}; representative examples with component designations, and cat/feed ratios for HY and HZSM-5 as in Fig. 2. Cat/feed ratio for reaction on the zeolite combination = 0.1870 and time-on-stream (a) 500 sec and (b) 840 sec.

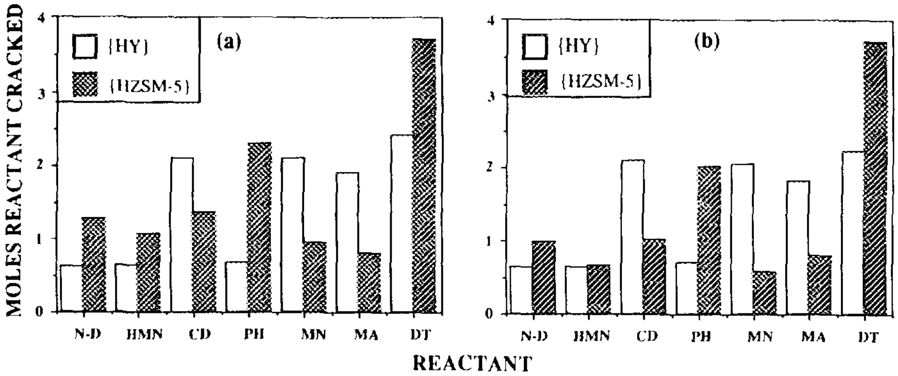

FIG. 4. Removal of feed components (accounting for feedstock molar composition) during reaction on HY and HZSM-5 at 400°C; component designations, reaction conditions, and cat/feed ratios as in Fig. 2, and time-on-stream (a) 500 sec and (b) 840 sec.

nent present in the original feedstock, as shown in Table 1, and also the reactivity of each hydrocarbon under the cracking conditions used. The rate of removal of each component will depend on the intrinsic reactivity of the molecular species and the rate of aging of active sites available for reaction. For a diverse mixture of hydrocarbons, there will be many types of reaction processes occurring, which may take place on different active sites (*9*, *16*). In the present study, we cannot separate these two factors, so that any comparison of conversions reflects both intrinsic reactivity of a component and the rate of loss of available sites for reaction of that component.

Figures 4a and 4b show distributions of feedstock components removed for reaction on both HY and HZSM-5, under identical cracking conditions for two different times on stream, by taking into consideration the feedstock molar composition (Table 1). The reactivity of the linear and branched paraffins on the faujasite is very similar, reflecting the rate of cleavage of a $-CH_2-CHR-$ unit in either molecule. Nace (*17*) suggests that the rate of dodecane cracking is about five times greater on REHX catalyst than that for heptamethylnonane when studied in isolation. The preferential reactivity of the linear paraffin on the pentasil reflects a shape-selective effect (*18*). Chen and Garwood (*19*), have previously shown that ZSM-5 exhibits shape-selective effects on large molecules such as alkylbenzenes and dimethyl-substituted paraffins. This may also explain the higher activity of the cycloparaffin on the faujasite compared to the pentasil.

An examination of the reactivity of the aromatic species (phenylheptane, methylnaphthalene and methylanthracene) shows that the one-ring system is most reactive on HZSM-5 and least reactive on HY. This may reflect a shape selective effect on the pentasil where the larger multiring hydrocarbon species cannot easily penetrate the pore system, as well as the selective removal of the larger aromatics on HY to produce coke. Anderson *et al.* (*20*) have suggested that naphthalenes and anthracenes may in fact react on the external surfaces of the pentasil. It is interesting to note that the minor component dodecahydrotriphenylene is the most reactive species when considered on a molar activity basis. This naphthene can be considered a structural relative of tetralin and may be expected to readily participate in hydrogen transfer processes (*25*), particularly on the faujasite. It is perhaps surprising to note that this component also has the highest reactivity on HZSM-5. The four-ring system might be expected to be excluded from the medium-sized pores (5.4 × 5.6 Å)

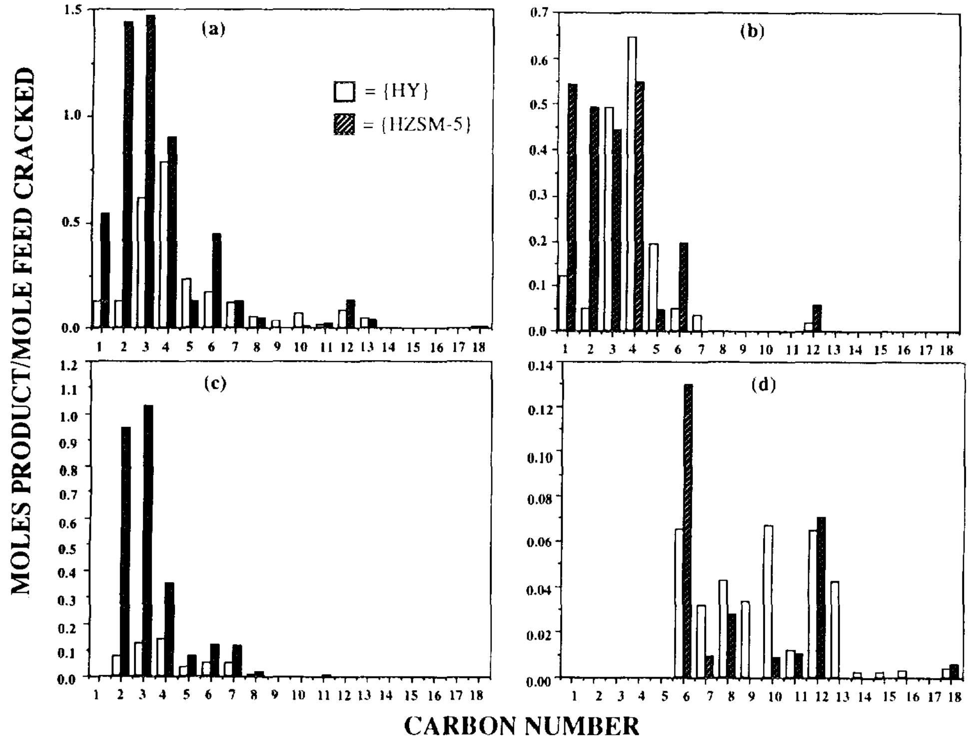

FIG. 5. Product distributions from reaction of feed on HY and HZSM-5 at 400°C. Representative examples with cat/feed ratios as in Fig. 2 and 500 sec TOS: (a) total hydrocarbons; (b) paraffins, (c) olefins, and (d) aromatics.

of the pentasil structure. Again, reaction on the external surface of the pentasil may occur. It has been shown, however, that large molecules (for example, esters typical in plant extracts) which can exhibit directional flexibility of bond angles are capable of penetrating the medium pores of the pentasil (*21*).

Appearance of Products

Product distributions on individual catalysts. Product distributions from reaction of the feedstock on HY and HZSM-5 at 400°C are shown in Figs. 5a–5d for total hydrocarbons, paraffins, olefins, and aromatics, respectively, corresponding to 500 sec TOS. Experiments carried out at other times-on-stream (ranging from 400 to 1200 sec) showed that the observed phenomena are independent of run duration. In these figures, it should be noted that the two product distributions are obtained at significantly different levels of conversion, 30% on HY compared to 8% on HZSM-5. Over 130 individual product species were identified ranging from methane up to C_{18} aromatics.

Figure 5a shows a higher selectivity towards hydrocarbons of lower molecular size, particularly light gases, on HZSM-5. This shift in product molecular size has also been reported for cracking of individual paraffin feedstocks on these zeolites (*22, 23*). This feature has been attributed to the low acid-site density (hence stronger acid sites) of the HZSM-5 zeolite due to its high Si/Al ratio (*23*). The overall product paraffin-to-olefin ratios (P/O) shown in Table 2 reflect the increased tendency towards hydrogen transfer processes on HY (*24*). For reaction on HY, the total P/O ratio is in excess of 1 (ranging from 1 to 3.4), while that on

TABLE 2

Comparison of Paraffin-to-Olefin Ratios for Cracking Products on HY and HZSM-5

TOS (sec)	{HY}		{HZSM-5}		{Y + Z}[a]	
	Cat/feed ratio	P/O	Cat/feed ratio	P/O	Cat/feed ratio	P/O
270	0.0404	1.01	0.0019	0.74	0.0423	0.99
510	0.0404	1.21	0.0019	0.86	0.0423	0.86
840	0.0404	1.24	0.0019	0.89	0.0423	0.82
1020	0.0404	1.29	0.0019	0.96	0.0423	0.79
270	0.1780	2.92	0.0090	0.81	0.1870	1.72
500	0.1780	3.31	0.0090	0.86	0.1870	1.72
840	0.1780	3.24	0.0090	0.79	0.1870	1.60
1000	0.1780	3.43	0.0090	0.79	0.1870	1.68

[a] Combination of faujasite and pentasil zeolites.

HZSM-5 is less than 1 (ranging from 0.7 to 0.9). Higher propensity towards hydrogen transfer is also shown by the higher tendency to produce aromatics on HY, as illustrated in Fig. 5d.

Due to the low aromatic yields reported from cracking of *n*-dodecane and cyclododecane (*17*), it is reasonable to assume that the relatively high proportion of aromatic products observed for our mixed feedstock arises directly from reaction of feed aromatics. The molar amounts of one-, two-, and three-ring aromatic species removed from the feed were compared with the corresponding molar product yields. While one- and three-ring aromatic species were produced, the proportion of two-ring aromatic systems decreased for cracking on HY, HZSM-5, and the zeolite combination. This suggests that two-ring aromatic species present in the feed may react to produce excess one- and three-ring species, as well as acting as preferential coke precursors, particularly on the faujasite. It is also possible that olefin oligomerisation processes, especially on the HZSM-5, could lead to the production of additional aromatic species. The high yields of benzene and alkylated benzenes found on both catalysts in this study may be accounted for by reference to the work of Corma *et al.* (*25*), who reported high product selectivities for such species on cracking of 1-phenylheptane over USY catalysts.

Comparatively few studies have been presented on the cracking of naphthalenes and naphtheno-aromatic molecules, and their relative reactivity rates are not well documented. Many such species are solids, making it more difficult to study their cracking behaviour experimentally. Mostad *et al.* (*26*) recently proposed a series of reaction schemes to account for the observed cracking activity of tetralin and decalin. Both naphthenic ring cleavage producing monoaromatics and dehydrogenation to naphthalene are important. The dodecahydrotriphenylene feed molecule may be assumed as being a structural relative of tetralin and hence similar reactions can be considered. Naphthalene was seen as a major product in our study, the source of which is considered to be predominantly from dealkylation of the 1-methylnaphthalene feed, and also possibly via dehydrogenation of the naphthene ring system. Mostad also suggests that ring opening processes (following hydride abstraction at the aromatic ring) may lead to the production of alkylated benzenes, such as those observed in this study. Complete elucidation of reaction pathways in the cracking of feed aromatic molecules in this study are not presently possible.

Almost all products identified were observed from reaction of the mixed feed on both catalysts. One exception, was the formation of styrene on HZSM-5, whereas this product was not found from the reaction on HY. Fukase and Wojciechowski (*27*) have also noted the production of styrene from the cracking of cumene on the pentasil but not on the faujasite. It is possible that hydrogen transfer processes on HY zeolite could lead to the rapid formation of ethylbenzene, whereas the decreased tendency for this process on the pentasil retards further reaction. The origin of styrene in the present study is uncertain. A decrease in the proportion of two-ring aromatic species has already been noted. Possibly cracking of 1-methylnaphthalene accompanied by hy-

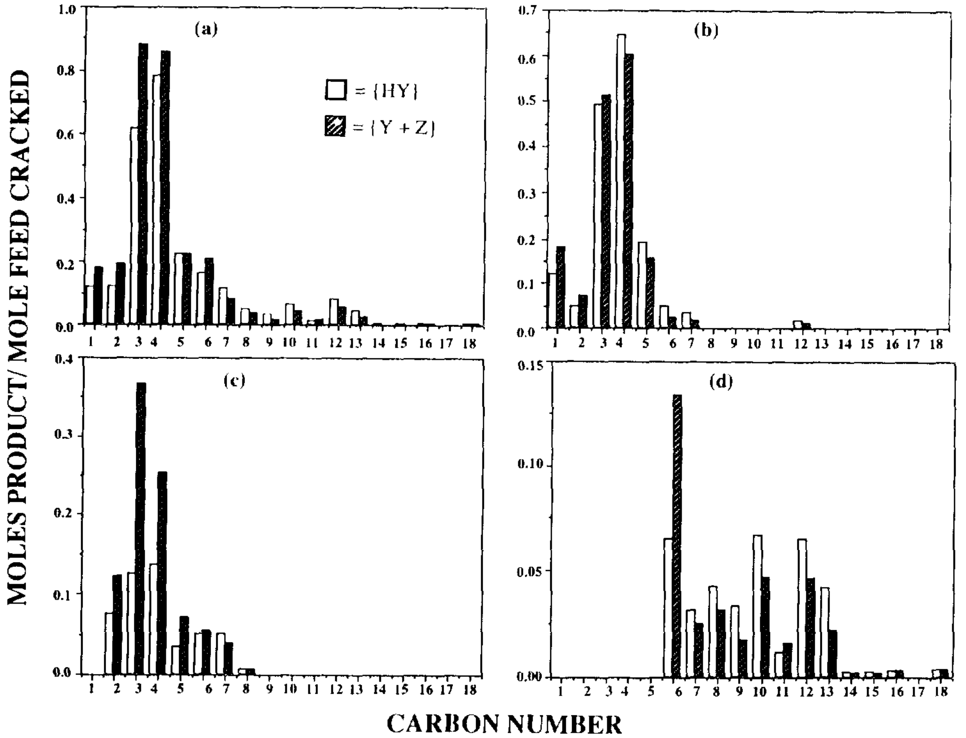

FIG. 6. Product distributions from reaction of feed on HY and zeolite combination at 400°C. Representative examples with cat/feed ratios for reaction on: HY = 0.1780; zeolite combination = 0.1870 and 500 sec TOS: (a) total hydrocarbons, (b) paraffins, (c) olefins, and (d) aromatics.

drogenation steps could lead to the formation of styrene and a C_3 olefin. Alternatively, the styrene may result from the cracking of the alkyl side chain of the phenylheptane species. However, a recent study by Corma *et al.* (*25*) found that styrene was not formed as a catalytic product on a Y zeolite from reaction of phenylheptane at 500°C, although it was detected as a thermal product.

Comparison of product distributions on HY and zeolite combination: The effect of the pentasil additive. The following discussion attempts to account for the effect of pentasil addition on the products formed on the faujasite zeolite. This is made difficult by the complex nature of the numerous possible reaction pathways. Figure 6a shows a typical product distribution for total hydrocarbons from cracking the feedstock on HY and also on the faujasite–pentasil combination designated by {Y + Z}. Comparing these product distributions, the most apparent differences are increased yields of C_3 and C_4 hydrocarbons with pentasil present. The total yields of C_1, C_2, and C_6 hydrocarbons are also increased with the zeolite combination, while there is a yield loss of C_7 to C_{13} hydrocarbons. Changes in product distribution in the presence of the pentasil additive can be attributed to either changes in the selectivity for feedstock component removal or the influence of the additive on the products themselves, particularly involving secondary reactions on the faujasite. Shifts in selectivity for cracking of feedstock components have already been presented in Fig. 3. Separating the total hydrocarbon product distribution into paraffin, olefin, and aromatic components, as shown in Figs. 6b, 6c, and 6d, respectively, also assists in tracing the origins of changes in product distribution.

The increase in small cracking fragments, particularly C_3 and C_4, can be partially explained on the basis of a higher selectivity for cracking feedstock components which would preferentially give these product species. Figure 3 shows a higher selectivity for cracking *n*-dodecane and phenylheptane at the expense of methylnaphthalene and cyclododecane. A simple calculation shows that, considering *n*-dodecane, cyclododecane, and phenylheptane cracking to produce only C_3 and C_4 alicyclic species, it is possible to account for 72% of the combined additional C_3 and C_4 species produced by the addition of HZSM-5 in Fig. 6a.

Figure 6b shows the product distribution for paraffinic species formed by reaction of the mixed feedstock on the pentasil/faujasite combination. For all carbon numbers, higher than C_3, there is a notable decrease in paraffin yield for reaction over the zeolite combination in comparison to the base faujasite catalyst case. This suggests that the pentasil additive acts to suppress bimolecular hydrogen transfer processes, which would otherwise occur readily on HY, consistent with the proposal by Rajagopalan and Young (*1*).

The olefin distribution (Fig. 6c), shows a significant increase in yield of olefinic species for almost every carbon number, particularly at C_3 and C_4. This is consistent with almost all studies where pentasil additives are used in gas-oil cracking (*1–3, 5, 8, 13*). Industrially, these olefinic species may be subsequently used as alkylate feed, thus offsetting the decreased gasoline yield obtained at the expense of improved octane-rating (*4–9*). This increase in propene and butene yields has been attributed to the preferential centre-cracking of feed paraffins on the pentasil (*2, 13*). It is possible that some extra olefins are produced from the C_4, C_5, and C_6 paraffins removed (as discussed above). By assuming that the excess C_4, C_5, and C_6 paraffins (as shown in Fig. 6b) produce the corresponding olefins, the distribution for total olefins on the faujasite {Y} would be as shown in Fig. 7. This figure is obtained by adding the excess paraffins to the original olefin distribution and shows that hydrogen transfer processes may account for the excess C_4, C_5, C_6, and C_7 olefin yields. This is not the case, however, for the C_3 olefin, such that processes other than hydrogen transfer must be involved. Calculation shows that suppression of hydrogen transfer processes by this mechanism can account for 27% of the excess olefin yields.

Calculating the overall paraffin to olefin ratio (P/O) for products on both HY and on the combined catalyst, as shown in Table 2, provides further evidence for the reduction of hydrogen-transfer processes on the zeolite combination. It can be seen that the P/O ratio for the individual Y zeolite is always in excess of that for the pentasil–faujasite combination. Thus, the strong tendency for the conversion of olefins to paraffins via hydrogen-transfer on the faujasite (as indicated in the previous section describing cracking on the individual zeolite) is reduced by the presence of HZSM-5. An alternative explanation for reduced P/O ratios may be due to the cracking and oligomerisation processes of paraffinic species with the subsequent formation of hydrogen (*28–30*), thereby producing more olefins at the expense of paraffinic species.

The distribution of total aromatics (Fig. 6d) shows that for almost all carbon numbers other than C_6 there is a decrease in the yield of aromatics for reaction over the zeolite combination. Thus, it appears that preferential benzene formation occurs at the expense of alkylated aromatics. A strong tendency to produce benzene from reaction of the mixed feedstock on the pentasil in isolation has been noted previously (Fig. 5d). This may be the result of aromatisation reactions of olefins (*19*) or dealkylation processes in which side chains are removed from aromatic feed molecules. The distribution of aromatics suggests that in the presence of the pentasil, dealkylation of alkyl-

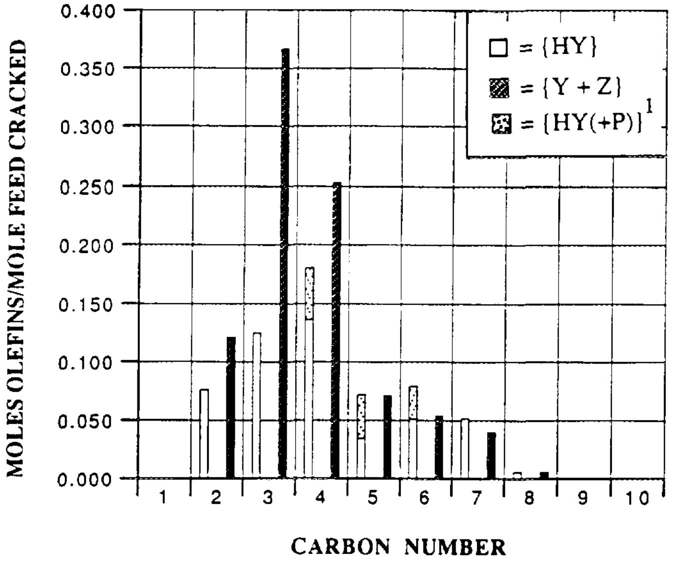

FIG. 7. Product distributions from reaction of feed on HY and zeolite combination, assuming extra paraffins produce olefinic species on HY. Conditions as in Fig. 6.

ated aromatics is enhanced. The removal of alkyl chains would contribute to the gain in C_2, C_3, and C_4 olefins and can account for 14% of the observed excess of these olefins in Fig. 6c.

It is generally reported (*2, 3, 8, 14*) that for cracking of gas-oil feeds, there is no net increase in aromatic yields, but a concentrating of such species on addition of HZSM-5. The fact that the total yield of aromatics (whether it be due to formation from aliphatic molecules or from isomerisation of feed molecules) is less than that on the base catalyst gives further support to decreased levels of hydrogen transfer on the zeolite mixture.

Figure 8 shows the comparison of branched to linear ratios (B/L) for C_4 and C_5 paraffins and C_4, C_5, and C_6 olefins produced by reaction of the mixed feedstock. This ratio for both C_4 and C_5 paraffins is less from reaction on the zeolite combination than that on HY. For C_4, C_5, and C_6 olefins, there is a slight increase in the ratio for reaction on the zeolite combination. The latter observation is in agreement with gas-oil studies (*2, 5, 6*), where faujasite–pentasil combinations also lead to increased B/L ratios for olefins. It has been suggested that preferential formation of branched olefins is due to isomerisation of normal carbenium ions, such that low octane linear olefins produce more highly branched, high-octane

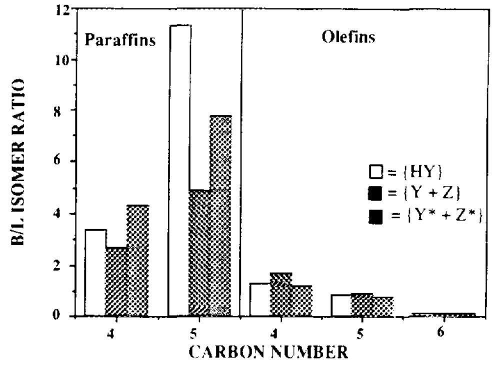

FIG. 8. Ratios of branched-to-linear paraffins and olefins from reaction on HY {HY}, a faujasite/pentasil zeolite combination {Y + Z} and calculated values for the combination {Y* + Z*}. Reaction conditions as in Fig. 3.

olefins. The observed shift in paraffin B/L ratios in Fig. 8 is, however, contrary to many gas-oil cracking studies on zeolite combinations. It has been widely reported (*3, 6, 8*) that low-octane linear paraffins are isomerised to more highly branched paraffins species. Other studies, however, report decreased B/L paraffin ratios (*1, 2*).

There have been conflicting reports on the effects of pentasil addition on the amounts of methane and ethane produced during gas-oil cracking (*1, 9, 13, 31*). Some investigators have reported no changes (*1, 13*) in the yields of these products. Figure 6a shows that for our mixed hydrocarbon feedstock, formation of C_1 and C_2 paraffins is increased, consistent with other investigations (*9, 31*).

Comparison of experimental and calculated product distributions. The approach described above, where the product distribution for feedstock cracking on a faujasite catalyst is compared with that on a faujasite–pentasil combination, is the one most commonly presented, particularly for studies on cracking of gas-oils (*1–9*). A calculated product distribution may also be obtained, by considering the relative contributions from the individual product distributions and conversions on the individual zeolite components. Effects resulting from the interaction of the products of one catalyst with the other in binary combinations can be identified by comparing the calculated and observed product distributions. This may allow us to deduce, for example, whether the reported increases in C_3 and C_4 cracking fragments for cracking of gas-oils with a pentasil additive is due mainly to the direct contribution of ZSM-5 to feedstock cracking, or whether the additive exerts an influence on the products arising from the faujasite.

Two methods for obtaining calculated distributions are presented here. In the first approach (Method 1), the predicted distribution, designated as $\{Y^* + Z^*\}$, is obtained by calculating a weighted value from the distributions on the individual zeolites at equivalent TOS. This approach assumes that the products formed on HY are unaffected by the presence of HZSM-5 and vice versa. In the second approach (Method 2), the difference in conversions between that observed on the zeolite combination and that on the faujasite catalyst is used to apply a weighting factor to the individual product distribution on the HZSM-5. This is then added to the individual distribution on the faujasite, giving the predicted distribution, designated as $\{Y + Z^*\}$. Any variation between observed and predicted distributions can be explained in terms of interactions and additional reaction processes.

Figures 9 and 10 show that the observed and calculated product distributions using either approaches to calculation are similar. Figures 9a and 10a show that for the total distribution of hydrocarbons, more C_3, C_4, C_5, and C_6 products are observed than predicted, at the expense of higher molecular weight species. Figures 9b and 10b show excess formation of C_3, C_4, and C_5 olefins, which can be attributed only partially to depletion in the corresponding paraffins (Figs. 9c and 10c). This corresponds to the reduction in hydrogen-transfer processes involving cracking products formed on the HY, so that fewer olefinic species are converted to the corresponding saturated products, as suggested during reactions of gas-oils (*18, 31*). Other potential sources of C_3 and C_4 olefins result from additional cracking of C_6 and C_7 olefins. Cracking of larger olefins to give higher yields of light olefins has also been suggested as a source of additional C_3 and C_4 olefins during cracking of gas oils using pentasil additive (*2, 14*). Figures 9d and 10d show that the total amount of aromatic species is similar to that predicted by calculation. However, there is a significant increase in the proportion of benzene at the expense of alkylated aromatics. The observed increased yield of benzene may be the result of preferential formation of the monoaromatic species on the pentasil zeolite or extensive dealkylation on the HZSM-5 of aromatic species initially

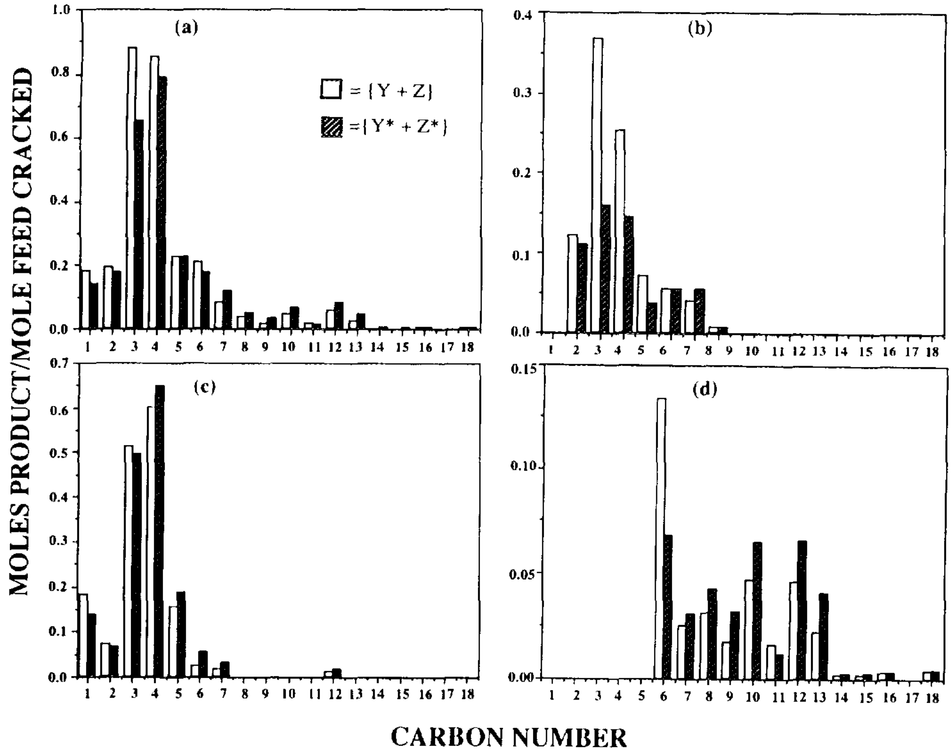

FIG. 9. Observed and calculated (Method I) product distributions from reaction of feedstock on a faujasite/pentasil combination at 400°C. Representative examples with cat/feed ratio for reaction on the zeolite combination = 0.1870 and 500 sec TOS: (a) total hydrocarbons, (b) olefins, (c) paraffins, and (d) aromatics.

formed on the HY. Alternatively, oligomerisation of light olefins (C_2 and C_3 species) to produce benzene as suggested by Dejaifve *et al.* (*32*) may also be a contributing factor. The extent of the relative contributions from any of these possibilities is difficult to ascertain given the complex nature of the feedstock. In either case, the side chains removed would appear as small olefins, which also contribute to the excess values seen in Figs. 8c and 9c. The increase in total C_6 hydrocarbons (Figs. 9a and 10a) results from the contribution from benzene.

Inspection of the B/L ratios for paraffins (Fig. 8) reveals that the predicted value is greater than observed on the zeolite combination for both C_4 and C_5 paraffins. There is only a slight variance between predicted and observed values for the C_4, C_5, and C_6 olefinic species. As the distribution of paraffins (Fig. 9c) shows that both C_4 and C_5 paraffins are produced in somewhat lower yields than predicted, it is possible to recalculate the predicted ratios of B/L paraffin isomers to approach the observed values, giving adjusted values as shown in Table 3. In obtaining these adjusted values, the losses may be attributed to the selective cracking of branched paraffins. Such processes would require the formation of significant additional amounts C_1 and C_2 paraffins (*33, 34*), which is not apparent in Fig. 9c. This observation, together with the fact that the adjusted values cannot match the observed B/L ratios even if selective cracking is assumed, indicates that isomerisation of branched paraffins must occur.

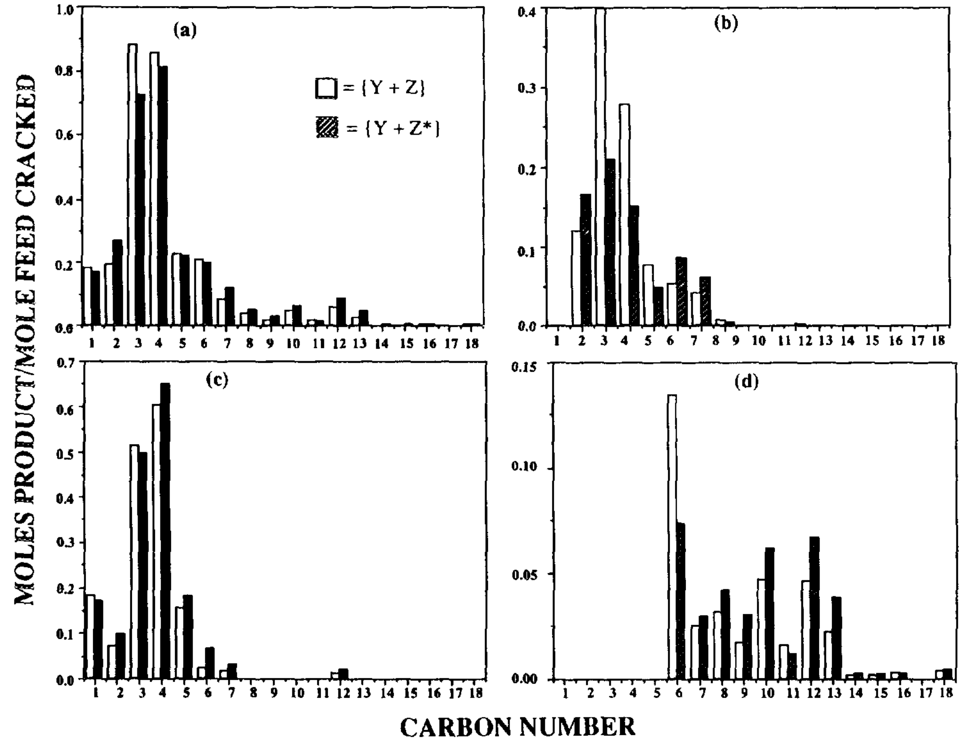

FIG. 10. Observed and calculated (Method 2) product distributions from reaction of feedstock on a faujasite/pentasil combination at 400°C. Representative examples with cat/feed ratio for reaction on the zeolite combination = 0.1870 and 500 sec. TOS: (a) total hydrocarbons, (b) olefins, (c) paraffins, and (d) aromatics.

CONCLUSIONS

The cracking of a complex hydrocarbon mixture as a model gas-oil feed on individual HY and HZSM-5 zeolites, and also on combinations of these, has been investigated. This allows the concurrent study of the removal of individual feedstock components as well as the appearance of product species. Many of the features previously reported during cracking of gas-oils using pentasil additives have been observed. These can be attributed to changes in selectivity for feedstock removal which gives rise directly to changes in observed product distributions, and also to interactions of product species from one zeolite with the other, particularly products from the faujasite interacting with the pentasil. The total influence of the pentasil can be seen by comparing the distribution from reaction on the faujasite and the zeolite combination, i.e., comparing {HY} and {Y + Z}. The effect of interactions of product species with the other zeolite can be resolved by comparing a calculated overall distribution based on an assumption of simple weighted addition {Y* + Z*} or {Y + Z*} with the observed distribution, {Y + Z}.

Increased amounts of C_3 and C_4 cracking products arise partly from preferential cracking of feedstock components favouring their formation, such as linear paraffins and *n*-alkyl benzenes. The presence of the pentasil increases the relative amount of olefins in the range C_4–C_7 by suppression of hydrogen-transfer processes that would have otherwise occurred during secondary processes involving products on the fauja-

TABLE 3

Ratios of Branched-to-Linear Paraffins from the Catalytic Reaction of Feed on Zeolite Combinations

TOS (sec)	Cat/feed ratio	Ratios of branched-to-linear isomers					
		C_4			C_5		
		Observed	Predicted[a]	Adjusted[b]	Observed	Predicted[a]	Adjusted[b]
270	0.0423	2.36	2.75	2.59			
510	0.0423	2.86	4.38	3.44	3.46	10.79	5.22
840	0.0423	2.65	4.31	3.95	4.88	7.77	6.49
1020	0.0423	2.47	4.36	3.28	5.09	6.22	5.44
270	0.1870	2.36	2.92	2.82	3.87	7.35	6.16
500	0.1870	2.50	3.25	2.95	4.04	5.91	4.71
840	0.1870	2.22	3.16	2.89	3.74	5.05	4.05
1000	0.1870	2.21	3.95	2.91	3.26	5.43	3.82

[a] The predicted value is calculated by assuming that proportional contributions for reaction on individual catalysts can be combined by simple addition.

[b] Adjusted values are calculated by assuming that the reduction in paraffin formation is accounted for by selective removal of branched saturated isomers.

site. Similarly, changes in the distribution of aromatics can be attributed to the dealkylation of aromatic species by ZSM-5 involving products formed on the faujasite, and this process also leads to additional olefins. The pentasil enhances the level of branching in olefinic species indicating formation of a greater proportion of branched olefin isomers through cracking processes on ZSM-5 and also isomerisation of linear olefins initially formed on HY. The addition of the pentasil, however, reduces the level of branching in small (C_4 and C_5) paraffin product species, again not only because of the preferential formation of linear saturated isomers during cracking processes, but also due to influences on the product distributions from the faujasite.

Previous studies of pentasil addition during cracking of gas-oils have reported increases in C_3 and C_4 species, particularly olefins, reduction in hydrogen-transfer processes and increased tendency to form branched olefins. In these respects, the hydrocarbon mixture studied here shows similar behaviour. An exception, however, is the increased tendency to produce linear paraffins from mixture, whereas the opposite is reported in some cases for gas-oils. Whether this is due to features associated with differences particular composition of the gas-oil and our test mixture is not yet clear.

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