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Catalytic Cracking of a Gippsland Reduced Crude on Zeolite Catalysts

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Cracking reactions of a Gippsland reduced crude have been investigated at 520°C over HY and HZSM-5. Gasolines with similar characteristics can be obtained on both zeolites, although the mechanistic routes to these products are quite distinct. Changes in aromatic product selectivities are consistent with the zeolite pore geometries. Minor quantities of aromatics are formed via hydrogen transfer processes involving product olefins and naphthenes over the faujasite and the cyclisation (and to a lesser extent oligomerisation) of olefinic species on the pentasil. Dehydrogenation of naphthenic species in the feedstock is also important for aromatic formation. While paraffins are formed via hydrogen transfer processes together with cracking and isomerisation of feed paraffins on HY, only the latter route can explain formation of saturated species on HZSM-5. The removal of linear paraffins from the GRC was traced as a function of conversion on HY. It was found that the relative reactivity of the linear paraffins increased monotonically with paraffin chain length. © 1994 Academic Press, Inc.

INTRODUCTION

There have been many reported studies on the cracking of both gas-oils (1–6) and pure hydrocarbons (7–9), which are believed to be representative of the components present in the complex industrial feedstocks. However, it is always a matter of conjecture as to whether reactions of pure compounds carried out in the absence of other classes of hydrocarbons are truly representative of their behaviour under industrial conditions. Furthermore, it is also almost impossible to trace the origin of various product species from a gas-oil containing hundreds of individual components. There have been a number of recent investigations using relatively simple mixtures of various hydrocarbon types (10, 11). Cracking studies of mixtures which contain a homologous series of similar reactants, such as n-paraffins derived from Fischer–Tropsch synthesis (12, 13), have also been presented. This greatly simplifies the problem of attempting to trace the origin of specific product species.

In the present study, we have investigated the cracking reactions of a commercial reduced crude feedstock obtained from the Gippsland Basin (Australia). The major component of this highly paraffinic feedstock was a series of n-paraffins from C_{14} to C_{32}, clearly identifiable by GC separation, and the other components could be classified as mainly naphthenic, with very little aromatic character.

EXPERIMENTAL

The apparatus and techniques were similar to those used in previous cracking studies (10, 14) with an integral, fixed-bed gas phase plug flow reactor. The vertically mounted feed syringe was heated with infrared lamps to avoid solidification of the viscous fluid. The reactor contained a known amount of catalyst at 520°C, over which 5 g of feed was pumped at a constant rate, giving a feed time on stream of 270 s. To achieve higher conversion levels, the mass of catalyst was increased as required. Due to volume limitations in the reactor, it was possible to consider catalyst-to-feed ratios of up to 1.0 only. Fresh catalyst was used in each experiment, as the regeneration conditions used (520°C, flowing stream of air for 24 h) were found to be insufficient to restore the catalyst to its original activity.

The catalysts used were HY CBV 400 (Si/Al = 5.2; Na_2O = 3.11 wt%; surface area = 720 $m^2 g^{-1}$) and HZSM-5 CBV 1502 (Si/Al = 161.2; Na_2O = 0.02 wt%; surface area = 403 $m^2 g^{-1}$), both from PQ Zeolites (The Netherlands). Pure, unsteamed catalysts were used throughout this study. All catalysts (mesh size 40–125 μm) were calcined at 500°C prior to use.

For cracking experiments with model feedstocks, a series of n-paraffins, ranging from n-dodecane through to n-hexacosane, were obtained from Aldrich and used without further purification.

Product Analysis

Three separate GC analyses were conducted to quantify the cracking products. Analysis of the gaseous product with a HP 5890A GC gave C_1–C_4 hydrocarbon products using a Chrompak capillary column (25 m × 0.32 mm

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TABLE 1

Characteristics of the Gippsland Reduced Crude (GRC)

	Elemental analysis	^{1}H NMR analysis[a]	^{13}C NMR analysis[b]	Physical properties
% C	85.85			
% H	13.74			
% N	0.10			
% O + S	0.31			
H/C Ratio	1.92	1.91	1.92	
Aromatics (%)		8.94	7.75	
Paraffins (%)		91.06	92.25	
Olefins (%)		0.00	0.00	
Aromaticity[c]		0.068	0.0775	
Naphthenic[d] (%)		18.08		
Density (g/ml at 15°C)				0.8646
Kinematic viscosity (100°C)				3.64
Ni (ppm)				<0.5
V (ppm)				<0.5
Conradson carbon (mass %)				0.95
Basic N (ppm)				200
UOP *K* factor				12.35

[a] From equations in Myers *et al.* (16).
[b] From equations in Clutter *et al.* (17).
[c] From the Brown–Ladner equation (15).
[d] From the equation $54.3(H_{CH_3}/H_{-CH_2-} + 0.100)$ (18).

i.d.), and molecular hydrogen using a molecular sieve 5A packed column and TCD. A simulated distillation analysis of the liquid sample enabled rapid quantification of gasoline range products. Simulated distillations of the liquid products were carried out on the same GC using a Supelco Petrocol 2887 SIMDIS capillary column (5 m × 0.53 mm i.d.), employing cryogenic cooling, and following ASTM method D2887. For a more accurate and detailed product analysis in the gasoline range, liquid products were analysed using a Hewlett–Packard 5890A gas chromatograph capable of electronic pressure programming with a Supelco DH capillary column (100 m × 0.25 mm i.d.) and flame ionisation detector. Hydrocarbon products were identified by a high resolution Kratos Concept S Series mass spectrometer.

Feedstock Characteristics

A Gippsland reduced crude (GRC) was obtained from Ampol Research and Development Laboratories, Lytton, Queensland (Australia). The reduced crude is the heavy oil left following distillation of gasoline, kerosene, and diesel fractions. Table 1 shows the composition as determined by elemental analysis and ^{13}C and ^{1}H NMR, and other physical properties.

The feedstock was highly paraffinic with an atomic H/C ratio of 1.92 from elemental analysis, and similar values were obtained by integrating either the proton NMR (H/C = 1.91) or the ^{13}C NMR (H/C = 1.92). Using the Brown–Ladner equation, the aromaticity of the sample via ^{1}H and ^{13}C NMR spectroscopy (15) gave values of 0.068 and 0.077, respectively. Details of the NMR assignments are given in Table 1 using equations from Myers *et al.* (16), Clutter *et al.* (17), and Williams (18). The FTIR spectrum of the sample supports this finding with only an extremely weak absorption band in the ~1600 cm^{-1} region (aromatic functional groups).

The SIMDIS profile for the feedstock in Fig. 1a shows

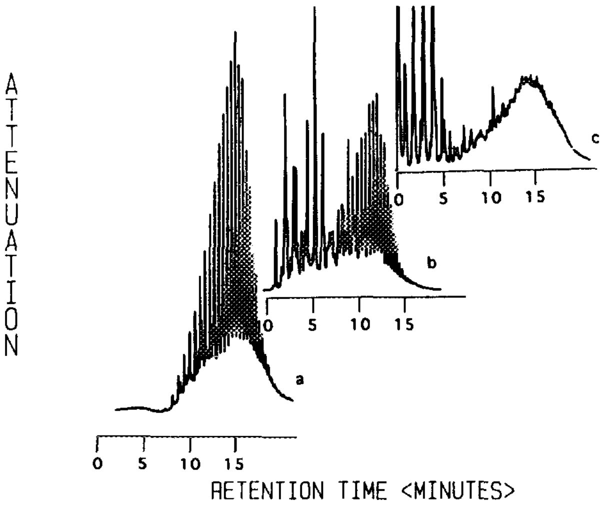

FIG. 1. SIMDIS profiles for (a) GRC feedstock, (b) product over HY at 520°C, and (c) product over HZSM-5 at 520°C.

the n-paraffin series typical of a wax. The UOP K factor of 12.3 indicates a highly paraffinic feed, as the UOP K factor is a measure of the aromatics content of the feed (19). Accurate ion-high-resolution mass spectrometry of the heavy crude revealed the presence of 2-ring (naphthalenes), 3-ring (anthracenes/phenanthrenes), and 4-ring (pyrenes) aromatic species, together with their respective alkylated isomers. Monoaromatic species, however, were almost entirely absent. Doubly branched di- and triaromatics were the predominant isomers in their respective series. Linear paraffins were detected from n-C_{14} up to n-C_{32}, with a maximum concentration at n-C_{25}. From gas chromatography, the n-paraffin content of the GRC was estimated at ≈64%. Monocycloparaffins with one alkylated substituent were also present in the feed.

RESULTS AND DISCUSSION

The degree of feed conversion was defined as the wt% of {gasoline + gaseous products + coke} (6). All yields quoted have been calculated on a wt% of feed basis. Figure 2 shows that conversion of the GRC increased with catalyst-to-feed ratio (C/F) on HY, approaching 75% at the highest C/F ratios. At equivalent C/F ratios, conversions on HZSM-5 were higher than on HY, increasing rapidly up to ≈65% conversion, then levelling off. This represents complete removal of the n-paraffins and provides evidence of a shape-selective effect for reaction on HZSM-5 (20).

Higher yields of both C_1–C_4 hydrocarbons and molecular hydrogen were observed on HZSM-5 compared to HY, due to lower acid-site density (hence stronger acid sites) on the pentasil (21). Propene, propane, and isobutane were produced in the largest yield. The observed paraffin to olefin ratio (P/O) for gaseous products (C_2, C_3, and C_4) was much higher on HY than on HZSM-5 for a given conversion level, as shown in Table 2 at 60.7% conversion. This is due to the enhanced hydrogen transfer potential on HY relative to HZSM-5 due to its low Si/Al ratio, producing adjacent active acid sites (22).

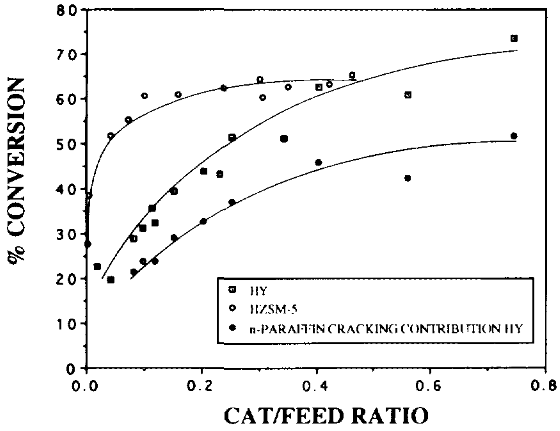

FIG. 2. GRC conversion at 520°C as a function of catalyst-to-feed ratios for cracking on HY and HZSM-5 and contribution to conversion from n-paraffin removal on HY.

TABLE 2

Paraffin to Olefin (P/O) Ratios for C_2–C_4 Gaseous Products from Cracking of GRC on HY and HZSM-5 at 520°C[a]

	Catalyst	
P/O ratio	HY	HZSM-5
C_2	1.34	0.17
C_3	1.41	0.17
C_4	2.60	0.21

[a] Conversion = 60.7%.

At comparable levels of conversion on HY and HZSM-5 (≈62%), the relative preference towards hydrogen transfer on the HY is also indicated by the paraffin-to-olefin ratio (P/O) for gasoline range products. Over the complete range of conversions, the gasoline P/O ratio on HY is higher than that on the pentasil and is found to increase with conversion, as shown in Table 3. The increase with conversion is due to the fact that hydrogen transfer is a consecutive process in which primary olefins become saturated. For hydrocarbons in the range C_7–C_{12} produced on HZSM-5, the observed yield of paraffins is higher than that for olefins, due to the formation of predominantly normal paraffin isomers.

For cracking of the GRC on HZSM-5, the yield of propene and propane is the highest of gaseous products, suggesting that if a carbonium ion mechanism is postulated, cracking is continued down to the smallest molecule possible (23). Selectivity plots for methane, ethene, ethane, and H_2 gases formed on HY (Figs. 3a–3d), show that these are all primary products (24). Corma *et al.* have

TABLE 3

Paraffin to Olefin (P/O) Ratios at Varying Conversions for Total Reaction Products from Cracking GRC over HY and HZSM-5 at 520°C

	P/O ratio	
% conversion	HY	HZSM-5
28.9	0.9	0.3
39.3	1.5	0.5
51.4	1.7	0.5
60.8	2.1	0.5
62.5	2.2	0.4

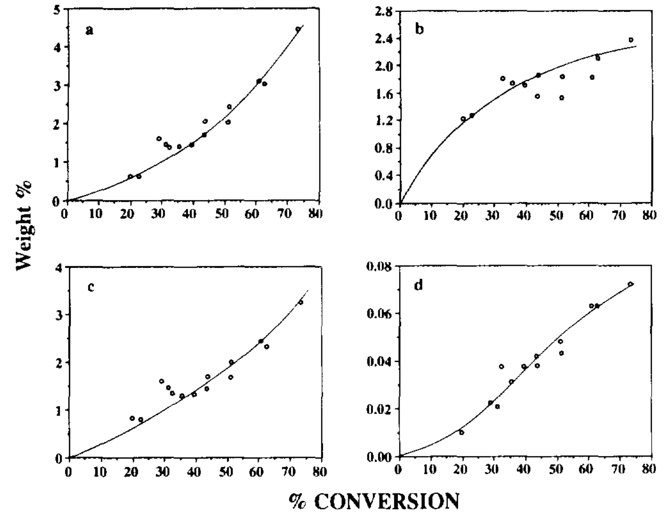

FIG. 3. Yield-conversion plots for light gases produced from the reaction of GRC on HY at 520°C: (a) methane, (b) ethene, (c) ethane, and (d) hydrogen.

shown that for the cracking of a vacuum distilled gas-oil over a REHY ultrastable zeolite in the temperature range 480–520°C, these gaseous products are all secondary (25). They thus suggest that rather than formation of a carbocation at a Brønsted site, initiation of the cracking process must occur via hydride abstraction by a Lewis acid site followed by β-scission processes. Our results suggest that it is indeed the carbonium ion mechanism (involving Brønsted acid sites) which applies to initiation of the reaction in this system, although some contribution from Lewis acid sites or thermal processes may also occur.

The simulated distillation profiles for typical cracking products on HY and HZSM-5 are shown in Figs. 1b and 1c, respectively. The formation of gasoline range products (C_5–C_{12}) at the expense of linear paraffins and naphthenic or aromatic species present in the feed is evident. Of particular note is the profile for cracking of the GRC on HZSM-5 (Fig. 1c), which is comparable to that obtained upon catalytic dewaxing of paraffinic feedstocks (26). The preferential removal of linear paraffins from the feed is apparent, while the bulkier naphthenic and aromatic species are much less reactive (27).

From the simulated distillation, it is possible to separate the liquid cracking product into various boiling range fractions. The gasoline fraction is defined as being in the C_5–C_{12} range (up to a boiling point of 216°C), while the light cycle oil (LCO) range is for hydrocarbons between C_{12} and C_{18} (216–316°C). The clarified oil is that fraction of the cracking product with a boiling point in excess of 316°C. Figure 4a shows that the yield of gasoline obtained from reaction on HY increases with the degree of feed conversion up to ≈65% conversion. A marked decrease in gasoline yield is noted as the degree of feed conversion increases above 65% conversion. This represents overcracking of the GRC feedstock, where gasoline yield is decreased by secondary cracking to C_3 and C_4 gaseous products. Similar results have been shown by Biswas and Maxwell (27) for cracking of an Arabian Heavy feed over USY catalyst at 520°C, John and Wojciechowski (28) for cracking of a neutral distillate over LaY catalyst at 503°C, and Corma *et al.* (25) for cracking of a vacuum gas-oil over REUSHY zeolite in the temperature range 480–520°C. A similar trend was found for reaction on HZSM-5. The origin of this increase is shown graphically in Fig. 4b, where the clarified oil fraction ($>C_{18}$) decreases markedly with conversion, while the LCO yield decreases only slightly with conversion. The feed had no gasoline range species, but is particularly concentrated in the C_{17}–C_{29} range; hence, this result may be expected.

While the SIMDIS analysis provides a rapid determination of gasoline yield, it does not produce an accurate product analysis. Therefore, a third GC was conducted on a fused-silica capillary column, with particular attention given to product species in the gasoline range, although major peaks located in the other fractions (LCO or clarified oil) were also considered. Products observed on both HY and HZSM-5 included paraffins (both branched and linear), olefins (branched and linear), naphthenes (saturated and unsaturated), and aromatics (alkylated mononu-

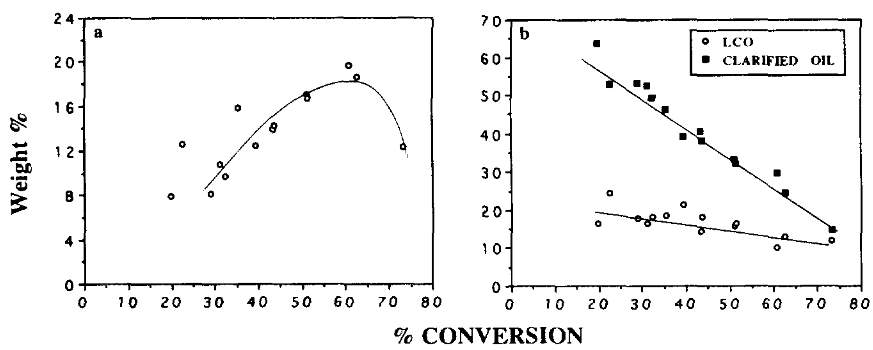

FIG. 4. (a) Gasoline and (b) light cycle oil and clarified oil yields as a function of conversion for cracking of GRC on HY at 520°C.

TABLE 4

Characteristics of Gasoline Produced from Cracking of GRC over HY and HZSM-5 at 520°C

Catalyst	% convsn.	Alkylate yield (%)[a]	Gasoline yield (%)[b]	GC-RON[c]	Aromatics (wt%)	Paraffins (wt%)	Olefins (wt%)	Naphthenes (wt%)
HY	62.5	28.84	18.6	90.5	13.51	2.85	1.55	0.74
HZSM-5	62.5	32.75	16.2	91.7	9.94	4.17	2.08	0.00

[a] Alkylate yield = wt% of C_3 + C_4 gaseous products.

[b] Gasoline fraction defined as C_5–C_{12} range.

[c] GC–RON values calculated using the Anderson–Sharkey–Walsh method (29).

clear and polynuclear species) and were classified into some 70 groups. The chromatographic resolution obtained yielded a detailed PONA (paraffin–olefin–naphthene–aromatic) analysis of the gasoline fraction.

Gasoline Characteristics

At conversion levels close to the limiting value obtained on HZSM-5 (i.e., ≈65%), gasolines of similar yield, composition, and octane rating may be produced on both catalysts as shown in Table 4 and Fig. 5. Although the overall gasoline yield on HZSM-5 was lower than on the faujasite, the potential alkylate yield from C_3 and C_4 gases is slightly higher on the pentasil. Such species may be used as feed for alkylation units to supplement the gasoline yield (6). At the high levels of conversion considered in Table 4, the overall gasoline composition is also quite similar, with a higher proportion of aromatics on HY together with lesser quantities of paraffins, olefins, and naphthenics. However, the mechanistic route for gasoline production differs on the two catalysts, as suggested by the variation in PONA composition with conversion, as shown in Fig. 6.

Via the detailed PONA analysis conducted here, a GC–RON value can be calculated using the method of Anderson *et al.* (29). The blending octane factors for each group have been modified to match the engine method for Ampol's gasoline. Figure 5 shows the GC–RON values for gasolines formed over HY and HZSM-5. The octane ratings for the products formed over HY are in the 83–90 octane range and increase with conversion. The origin of this GC–RON increase on HY may be traced to the production of olefins and aromatics, both known octane enhancers. An increase in the production of paraffins was also noted to cause an increase in GC–RON. This may seem at first to be an inconsistency, as paraffinic species are generally detrimental to octane rating. However, as discussed later, the gasoline range paraffins formed over HY are predominantly branched.

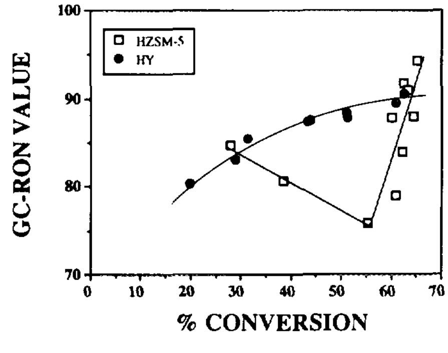

FIG. 5. Effect of GRC conversion on GC–RON of gasolines formed on HY and HZSM-5 at 520°C.

A quite different trend is noted for the influence of conversion on GC–RON for reaction on HZSM-5. The GC–RON value decreases by ~10 numbers over the conversion range 0–55%. As the level of conversion increases above this value, the GC–RON shows an increase of some 20 numbers over a conversion interval of 10%. This behaviour may be explained from the PONA plot for reaction of the GRC over HZSM-5. Up to a conversion level of 55%, linear paraffins are formed in high yields, while aromatics are produced in very small yields; at the same time, the olefin yield decreases. Above 55% conversion, the *n*-paraffins and olefins are cracked away whilst the yield for aromatics increases.

The Origin of Product Species

Figure 7 shows the product distributions from reaction on HY and HZSM-5 considering the combined (gas + gasoline) range. When tracing the origin of various product classes, it is important to recall the highly paraffinic nature of the feedstock (Table 1). On HZSM-5, paraffin reaction must be the dominant source of product species, leading to the observed ceiling illustrated in Fig. 2. For reaction on HY, although paraffins are the major source of product species, the naphthenic component of the feedstock also provides a significant contribution, as illustrated in Fig. 1. From the GC analyses, the *n*-paraffins typically contributed about 70% to the total, while the naphthenic components contribute ≈30%.

Figs. 7a and 7b show, for each catalyst system, comparisons for cracking of the GRC with that of *n*-hexadecane at 520°C. This linear paraffin provides a reasonable representation of the linear paraffin component of the GRC

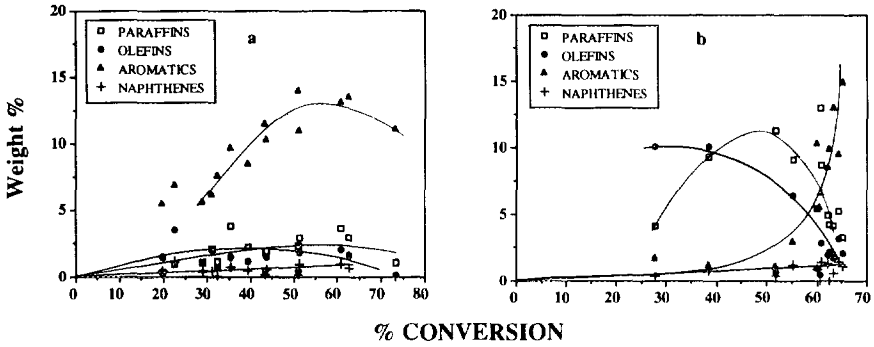

FIG. 6. PONA analyses for gasoline range products formed from the reaction of GRC on (a) HY and (b) HZSM-5 at 520°C.

feedstock. On both catalysts, the formations of paraffins, olefins, naphthenes, and aromatics are considered to be separate product classes.

For reaction on HZSM-5 (Fig. 7b), there is a close correlation between the product distribution for both feedstocks. Paraffins and olefins are the major initial species formed. Naphthenes and aromatics were only detected in trace amounts at low conversions. The major difference in behaviour between the two feedstocks lies in the significantly increased abundance of aromatics from reaction of the GRC at higher conversion levels, which may be associated with the apparent decline in stability of the olefins as the conversion level exceeds 50%.

Figure 7a shows that there is much lower overall correspondence between PONA product profiles for reaction of the two feedstocks on HY. While olefins and paraffins are again the major product species, significant amounts of aromatics are observed from the reaction of the GRC, even at relatively low levels of conversion.

Aromatics Formation

The degree of aromaticity of the GRC feedstock was low, with typical aromatics comprising 2- and 3-ring alkylated species and no alkylated monoaromatics. Van Klink *et al.* (30) have examined the origin of gasoline range aromatics during reaction of a gas-oil and have suggested that they may be formed either by alkylation of feed aromatics, by cyclisation and dehydrogenation of other gasoline range species, through aromatisation and dealkylation of naphthenic compounds, or via oligomerisation of olefins. The predominant reactions of polyaromatics under cracking conditions are isomerisation and disproportionation, so that monoaromatics cannot easily be formed via cleavage of polyaromatic species (31). Table 5 shows the distribution of aromatic species observed at high conversion from the GRC on both catalysts. On HY, the percentages of tri-, tetra-, and pentamethylbenzenes are higher than that of the shorter chain alkylaromatics (43.65%, cf. 40.42%). However, for HZSM-5, benzene, toluene, and the xylenes are produced preferentially (72.92%, cf. 19.48%).

Figure 7b clearly shows that aromatics are formed as secondary products from reaction of both the GRC or *n*-hexadecane on HZSM-5. The reaction of the paraffin component of the feedstock may account for only 1% of the aromatics yield. Figure 7b also suggests that on HZSM-5, oligomerisation of light olefins play a significant role in aromatic formation during reaction of the GRC at higher conversion levels. Cyclisation and aromatisation of gasoline range olefins is also important. These processes contribute to ≈95% of the observed aromatic yield at high

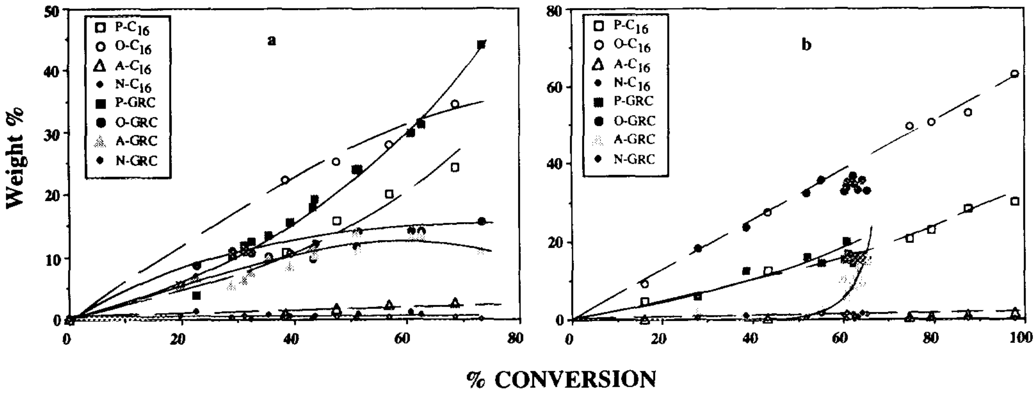

FIG. 7. Comparison of PONA products from the reaction of GRC (—) and *n*-hexadecane (---) on (a) HY and (b) HZSM-5 at 520°C.

TABLE 5

Gasoline Range Aromatic Species from Cracking GRC over HY and HZSM-5 at 520°C[a]

Aromatic species	Composition (wt %) HY	Composition (wt %) HZSM-5
Benzene	1.5	6.7
Toluene	12.2	27.4
Ethylbenzene	2.8	5.7
ortho-Xylene	6.6	4.4
meta-Xylene	11.7	9.7
para-Xylene	5.6	19.0
C3–C5 alkyl benzenes	43.6	19.5
Indan, C1-C2 alkyl indans	9.4	5.3
Naphthalene	6.5	2.3
Total	100.0	100.0

[a] Conversions of 60.7%.

conversions, which is evident from the sudden divergence of yield for olefins on the GRC compared to the *n*-hexadecane yield at conversions approaching 60%. However, the naphthenic component of the feedstock also appears to participate in the process leading to the formation of aromatics, perhaps providing a sink for hydrogen which must be accounted for during aromatisation of olefins. The extent to which naphthenic structures present in the GRC can react to produce gasoline range aromatics is difficult to define; however, by comparison with the reaction of *n*-hexadecane, this process may contribute less than 4% of the overall aromatics yield.

In contrast, for reaction of the GRC on HY (Fig. 7a), aromatics are formed as primary as well as secondary products, while they are clearly only formed as secondary products from the reaction of *n*-hexadecane. The naphthenic components of the feedstock appear to be the major source of aromatics. In comparison with data for the cracking of *n*-hexadecane, dehydrogenation of feed naphthenes may contribute as much as 85% to the observed aromatic yield. The formation of aromatics from the paraffin component of the GRC may account for 15% of the observed yield. Hydrogen transfer processes on the faujasite involving the combination of product olefins with unsaturated naphthenes (32) may also contribute to the formation of aromatic species. Both hydrogen transfer and dehydrogenation involve the transfer of hydrogen, and although hydrogen is observed as a reaction product, the quantities are insufficient to provide a simple balance. Instead, some of the available hydrogen must react with olefinic species to produce, in particular, gas range paraffins.

The levels of coke observed over the faujasite were higher than on the pentasil zeolite. This is a well-known observation (33, 34), and may be linked to the restriction of the formation of coke precursors in the small pores of HZSM-5. The presence of di-, tri-, and tetra-aromatic structures could lead to the formation of coke. Such large aromatic structures are known precursors to coke formation. Whilst such molecules may be admitted to the pores of the faujasite and thereby poison active sites or, alternatively, block the pores, this is not the case on the pentasil due to shape-selective effects (34).

Figures 8a and 8b summarise reactions during cracking of the GRC on HY and HZSM-5, respectively. The contribution to the formation of observed products from feedstock components (*n*-paraffins, naphthenes, and aromatics) is considered to be a function of feed conversion. The numbers in brackets represent an approximate contribution to the product formation based on the assumption that *n*-hexadecane is representative of *n*-paraffins in the GRC. Any difference between the product yields from

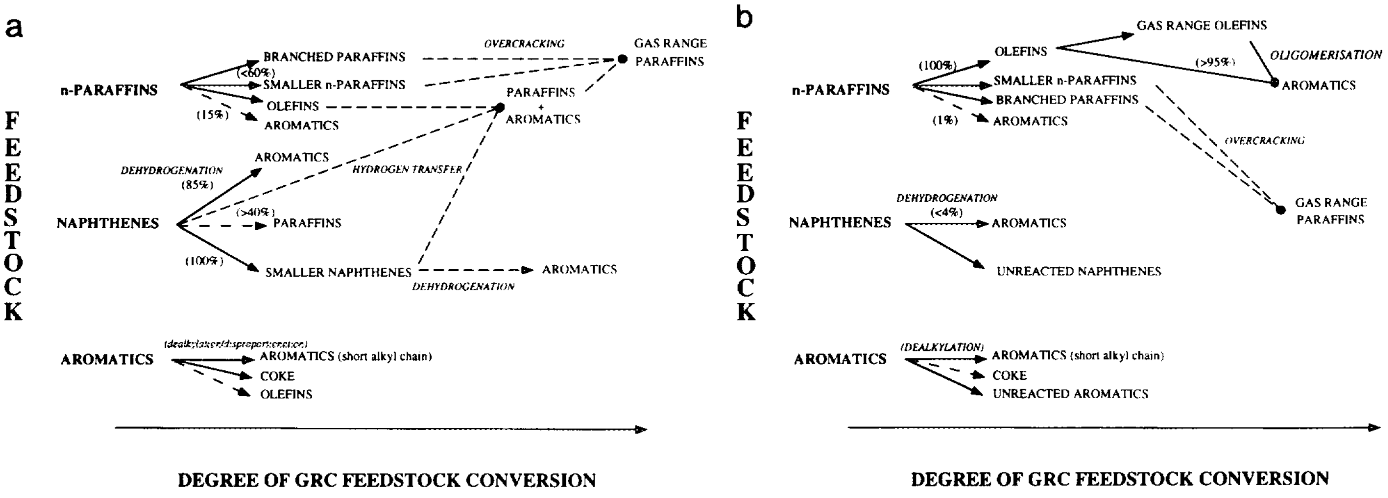

FIG. 8. (a) Reaction processes for GRC feedstock components on HY. (b) Reaction processes for GRC feedstock components on HZSM-5.

reaction of the GRC and *n*-hexadecane is assumed to be due to reaction of the naphthenic component of the GRC.

It is perhaps pertinent to point out that the product distributions discussed here are obtained over fresh catalyst. The reaction processes occurring over equilibrated refinery catalyst may be different. For example, Buchanan (35) has shown that *n*-paraffins in the range C_6–C_{10} are converted <1% over steamed HZSM-5. However, on nonsteamed catalyst, the conversion levels are appreciably higher. The observed high yields for benzene and the light gases for reaction of the GRC over HZSM-5 may also be due to the use of fresh catalyst. Also, a fixed-bed reactor is used in our experiments, with integral averaged conversion. The average conversions and product distributions presented herein do not reflect commercial riser data, for which products may be converted by deactivated catalyst. We do feel, however, that a study such as this serves to illustrate the reactions of a reduced crude over two distinctly different catalyst types.

Branched to Linear Ratios of Paraffins and Olefins

A critical factor which influences the octane rating of a gasoline is the degree of branching of its constituent molecules. Branched-to-linear ratios (B/L) for various product species are shown in Tables 6 and 7 and Figs. 9a and 9b. Table 6 shows that these ratios are not greatly influenced by feedstock conversion. For reaction over HY, the B/L ratio for paraffins is greater than 1 for all carbon numbers. The corresponding ratio on HZSM-5, however, is less than unity in all cases (Fig. 9b). One explanation for this may be that the precursors necessary for the production of branched isomers are prevented from forming in the narrower pores of the pentasil.

As regards other feedstocks, B/L ratios for paraffin products are consistently higher on HY than is observed for reaction on HZSM-5, as shown in Table 7. The actual magnitude of the B/L ratios, however, are feedstock dependent. The B/L ratios on HY for the GRC are intermediate between those obtained on *n*-hexadecane and on a severely dehydrogenated coal derived liquid CDL (36). For reaction on HZSM-5, however, the B/L ratios for the GRC more closely resemble those of the linear paraffin. The CDL employed was highly naphthenic in nature and may be considered representative of the naphthenic component of the GRC used in this study.

Table 7 shows B/L ratios of olefinic products are higher on HZSM-5 than the corresponding values on HY, irrespective of the feedstock composition. In contrast to the paraffins, the magnitude of the B/L ratio for olefin isomers lies generally in the range 1–2.5 and is not altered significantly by the feedstock type. This may perhaps be due to the high reactivity of olefins. Once formed, skeletal rearrangement of the carbenium ion occurs more rapidly than β-scission or hydrogen transfer. Thus, olefin species are formed via this fast isomerisation reaction irrespective of the feedstock composition, resulting in fairly similar B/L ratios.

This would suggest that together with the traditional carbenium ion rearrangement of linear alkanes to form branched saturated species (and typical of that found in *n*-hexadecane cracking), branching of products from naphthenic species is an important process, particularly on HY. The presence of alkylated naphthenes in the feed-

TABLE 6

Branched-to-Linear Ratios for C_4, C_5, and C_6 Products Formed from Reaction of GRC over HY and HZSM-5 at 520°C

	Ratio of branched-to-linear isomers											
	Paraffins						Olefins					
	C_4		C_5		C_6		C_4		C_5		C_6	
Wt% convsn.	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5
31.2	2.79		7.87		6.16		1.42		1.35		0.81	
35.5	2.88		10.12		7.20		1.32		1.55		1.02	
39.3	2.71		7.43		5.75		1.33		1.27		1.05	
43.7	2.53		6.86		3.68		1.33		1.39		1.89	
51.4	2.81		7.92		4.70		1.21		1.47		1.43	
62.5	2.56		6.86		4.55		1.32		1.76		1.54	
27.7		0.22		0.85		0.67		1.52		1.55		1.28
38.4		0.30		0.66		1.30		1.22		1.78		1.09
55.3		0.53		0.47		0.37		1.57		1.95		1.56
60.7		0.66		0.62		—		1.54		2.00		—
62.3		0.81		1.09		0.52		1.47		2.43		—
64.4		0.89		0.88		0.93		1.46		2.21		1.62

TABLE 7

Comparison of Branched-to-Linear Isomer Ratios for Cracking Products from *n*-Hexadecane, GRC, and CDL on HY and HZSM-5

	Paraffins						Olefins					
	C_4		C_5		C_6		C_4		C_5		C_6	
Feed	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5	HY	HZSM-5
n-C_{16}[a]	1.71	0.44	2.80	0.48	2.81	0.31	1.23	1.45	1.62	1.94	1.42	1.62
GRC[b]	2.53	0.30	7.43	0.66	5.75	1.30	1.33	1.22	1.39	2.32	1.89	1.09
CDL[c]	3.09	4.90	25.2	16.02	12.4	3.29	0.87	1.56	1.26	2.36	—	—

[a] n-C_{16} is *n*-hexadecane feedstock. Reaction temperature = 520°C.

[b] GRC is Gippsland reduced crude feedstock. Reaction temperature = 520°C.

[c] CDL is a coal-derived liquid feedstock. Results from Townsend and Abbot, Ref. (36). Reaction temperature = 480°C.

stock may lead to high B/L ratios as a cleavage of the ring structure yields branched product species. Krause (32) has shown that as the degree of substitution of C_5 and C_6 naphthenes increases, so does their reactivity. If it is assumed that isomerisation of linear paraffins occurs via protonated cyclic intermediates, then it is possible that in a highly naphthenic feed, such intermediates are readily available. Martens and Jacobs (37) have discussed the formation of branched species via substituted cyclopentane and cyclohexane intermediates. Such bulky intermediates may be prevented from forming in the smaller pores of the pentasil, such that formation of branched species via β-scission and rearrangement of carbenium ions is the predominant process.

Feedstock Component Removal—The Reactivity of Feed n-Paraffins

One disadvantage in using complex hydrocarbon mixtures and industrial crudes as feedstocks is that it is virtually impossible to monitor the origin of product species. There have been very few cracking studies using mixtures of known representative molecules (10, 11) in which it was possible to monitor both the disappearance of all feedstock components as well as the appearance of products. For the GRC used in this study, a well-defined *n*-paraffin series was evident in the feed (Fig. 1). It was thus possible to monitor the net rate of removal of the *n*-paraffins in the range C_{18}–C_{31} for reaction on HY. This was not possible on HZSM-5 due to the rapid removal of all *n*-paraffins even at low catalyst-to-feed ratios.

The fraction of each *n*-paraffin converted (relative to the amount present in the original feed) was determined as a function of overall feed conversion. As shown in Fig. 10, the net rate of cracking increases with the chain length of the linear paraffin in the GRC feedstock.

Another approach to the kinetic analysis follows the treatment developed by Kissin (38), using the ratio of first order rate constants for cracking of an *n*-paraffin relative to a marker *n*-paraffin in the feed given by

$$k_i/k_T = \ln(1 - X_i)/\ln(1 - X_T), \qquad [1]$$

in which k_i and k_T are the rate constants for cracking of *n*-paraffin i or marker compound T, and X_i and X_T are the fractional conversion of paraffin i or marker compound T.

In our work, the *n*-paraffin of highest concentration, *n*-C_{25}, was chosen as the marker compound. Figure 11 shows a plot of the relative rate constants (from Eq. [1])

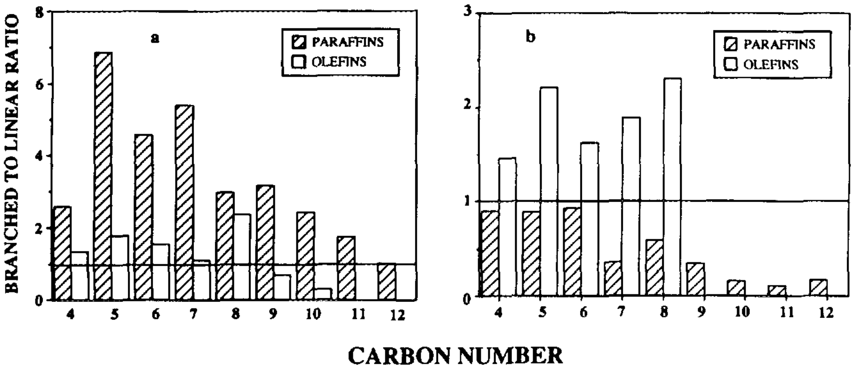

FIG. 9. Branched-to-linear ratios for product isomers from the reaction of GRC on (a) HY and (b) HZSM-5 at 520°C.

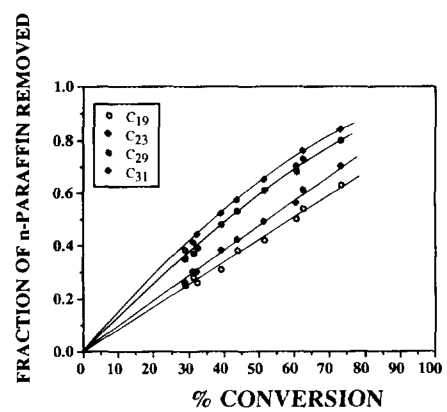

FIG. 10. Fraction of *n*-paraffin feed components removed as a function of conversion on HY at 520°C.

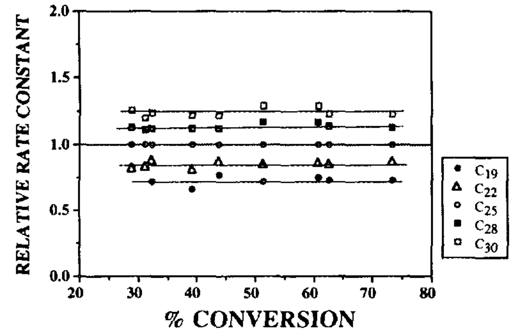

FIG. 11. Relative rate constants for representative *n*-paraffin GRC feed components cracked over HY at 520°C.

against overall feed conversion for paraffins in the range C_{19}–C_{31}. The calculated relative rate constants for *n*-paraffin removal increase with carbon number and are independent of conversion. This suggests that the net rate of cracking increased with the chain length of the *n*-paraffin. A similar result has been shown previously by Abbot and Wojciechowski (39) for the cracking of individual *n*-paraffins on zeolites. Both Kissin (38) and Nace (40) found that the relative reactivities of *n*-paraffins reacted in isolation increased up to C_{17} before levelling off. Voge (41) has shown that for the cracking of linear paraffins over a silica–alumina–zirconia catalyst at 500°C, the degree of conversion increased with carbon number, with only slight increases in reactivity above *n*-C_{20}. Liguras and Allen (42) calculated rate constants for *n*-paraffins in the range C_1–C_{25} and showed that the rate constant for the cracking of *n*-paraffins to carbenium ions and olefins (essentially the initiation of the cracking reaction) increases monotonically with carbon number.

The data presented for the removal of *n*-paraffins in the GRC feed may show a combined effect in which *n*-paraffins are both cracked and also formed from higher paraffin species in the feed; however, the extent to which this occurs in this feedstock cannot be easily determined. To better understand our results, two model feedstocks, one containing three *n*-paraffins, pentadecane ($C_{15}H_{32}$), eicosane ($C_{20}H_{42}$), and pentacosane ($C_{25}H_{52}$), and the other containing nine *n*-paraffins from *n*-dodecane ($C_{12}H_{26}$) through to hexacosane ($C_{26}H_{54}$), were prepared as shown in Table 8. Cracking of model feedstocks was studied over HY at 520°C (TOS = 270 s; C/F ratio = 0.0292). For reaction of both model feedstocks, negligible amounts of linear paraffins with chain length above C_{15} were detected as products. This implies that calculated

TABLE 8

Model *n*-Paraffin Feedstock Compositions and Reactivities for Cracking over HY at 520°C: Catalyst-to-feed Ratio = 0.0292

		Model feed compositions (mol % ratio)		*n*-Paraffin relative rate constants[d]		
Component	Formula	Feed 1[a,b]	Feed 2[a,c]	Feed 1	Feed 2	GRC
Dodecane	*n*-$C_{12}H_{26}$		30.27		0.100	
Tetradecane	*n*-$C_{14}H_{30}$		26.46		0.154	
Pentadecane	*n*-$C_{15}H_{32}$	94.83	26.25	0.065	0.191	
Eicosane	*n*-$C_{20}H_{42}$	1.48	11.22	0.418	0.582	0.774
Docosane	*n*-$C_{22}H_{46}$		0.74		0.787	0.848
Tricosane	*n*-$C_{23}H_{48}$		1.59		0.918	0.872
Tetracosane	*n*-$C_{24}H_{50}$		1.48		0.976	0.931
Pentacosane	*n*-$C_{25}H_{52}$	1.03	0.68	1.000	1.000	1.000
Hexacosane	*n*-$C_{26}H_{54}$		1.31		1.090	1.045

[a] Obtained via GC analysis.
[b] Impurities and 1-phenylheptane account for 2.66% of mol ratio.
[c] Impurities account for <0.1% of mol ratio.
[d] Obtained using Eq. [1] and in Ref. (38).

rate constants for linear paraffin removal using Eq. [1] can be taken as absolute rates of cracking for C_{20} and above. Comparison of the values in Table 8 shows that similar values are obtained under the same cracking conditions using model feedstock 2 containing only linear paraffins and the GRC when considering species in the range C_{20}–C_{26}. This suggests that the presence of other hydrocarbon types in the GRC does not significantly influence the relative rate of cracking of the linear paraffins present. Previous studies of cracking of individual linear paraffins on HY have suggested that the cracking rate (per crackable bond) increases in the range C_8–C_{16} (43). The present results show that this parameter continues to increase up to C_{32}.

CONCLUSIONS

Cracking reactions of a commercial feedstock containing a high proportion of linear paraffins, lesser amounts of alicyclic components, and low aromatic content have been studied on a faujasite and a pentasil. On HZSM-5, the dominant reaction is cracking of the paraffins, whereas on HY, reactions of other feedstock components are also significant. For cracking of this feedstock, gasolines with a similar quality can be produced on both zeolites. However, a detailed analysis of the gasoline range products and light gases, coupled with the disappearance of feedstock components, reveals that the routes leading to the gasoline species are distinctly different. Indepth studies of the cracking rates of the linear paraffins on HY have shown that reactivity continues to increase with chain length throughout the observed range.

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