THE INFLUENCE OF CATALYST AND FEEDSTOCK ON PRODUCT DISTRIBUTIONS FOR CRACKING OF C_8 PARAFFINS ON HY AND HZSM-5 ZEOLITES

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ABSTRACT

Catalytic cracking of n-octane and 2-methylheptane, as well as mixtures of these paraffins, has been studied on HY and HZSM-5 zeolites, and also on combinations of the catalysts. For cracking on individual zeolites, both feedstock and catalyst influence the resulting product distributions. For all feedstocks, product distributions are shifted towards smaller fragments for reaction on HZSM-5 compared to HY.

Ratios of branched to linear paraffins are much more strongly influenced by catalyst type and feedstock than the corresponding ratios for olefinic products. For reactions on catalyst mixtures, distributions of the total products by carbon number correspond well to a summation of contributions on the individual catalysts. However, a greater departure from prediction is seen for individual distributions of paraffins, olefins and aromatics, as well as for ratios of branched to linear paraffins, showing that hydrogen transfer processes and isomerization must occur. The addition of pentasil has also resulted in enrichment of the linear saturates at lower carbon number which is due to preferential cracking of linear paraffins over the branched isomers.

INTISARI

Reaksi pemecahan n-oktana, 2-metilheptana, dan campuran kedua parafin ini pada zeolit HY, zeolit HZSM-5, dan campuran kedua katalis telah dipelajari. Dalam reaksi pemecahan pada masing-masing zeolit, baik pereaksi maupun katalis keduanya mempengaruhi distribusi hasil reaksi. Distribusi total hasil reaksi pada zeolit HZSM-5 bergeser ke fragmen yang lebih kecil apabila dibandingkan dengan distribusi hasil reaksi pada zeolit HY, dan ini berlaku pada kedua parafin.

Perubahan ratio parafin bercabang/rantai lurus pada kedua katalis lebih peka dibandingkan perubahan ratio olefin. Dalam reaksi-reaksi pada campuran katalis, distribusi total hasil reaksi berdasarkan nomor karbon dapat disamakan dengan penjumlahan distribusi hasil reaksi dari kedua katalis secara terpisah. Namun demikian, terdapat deviasi yang menonjol pada distribusi parafin, olefin, dan aromatik. Penyimpangan juga terdapat pada ratio parafin bercabang/rantai lurus, yang kesemuanya menunjukkan terjadinya proses pemindahan hidrogen dan isomerisasi. Penambahan pentasil juga menyebabkan peningkatan jumlah parafin berantai pendek dan lurus sebagai hasil reaksi, ini disebabkan karena reaksi pemecahan parafin berantai lurus lebih mudah berlangsung daripada reaksi pemecahan parafin dengan rantai bercabang.

INTRODUCTION

The petroleum industry is one of the most important industry in the world today in term of the value of its final products. Many studies on the reactions of hydrocarbons on cracking catalysts have been undertaken since the commercial introduction of the catalysts. Most of these investigations have been concentrating on the cracking behaviour of hydrocarbons on single component catalysts. And to a lesser extent on combinations of catalysts.

Combinations of catalysts have been used during commercial cracking processes since the last decade. Numerous patents describe many different formulations of cracking catalysts, but the scientific literature contains much less information relating cracking phenomena of catalyst combinations to those of their components.

There has been recent interest in the effects of using combinations of zeolites as cracking catalysts. In particular, it has been found that addition of small amounts of HZSM-5 to HY zeolite can enhance the octane number of the gasoline produced [1-11]. Several explanations have been proposed to account for the effects of the pentasil additive during cracking of gas oils. Some investigators [1, 6] have suggested that there is a relative increase in the cracking of gasoline range linear paraffins, leading to higher proportions of the branched unsaturated isomers, contributing to a higher octane rating. Other investigator [8] reported that enhanced olefin cracking by the addition of HZSM-5, in preference to hydrogen transfer, would reduce formation of additional saturated products on the faujasite.

In spite of these studies, some of the principles are still under ongoing debate and are not clearly understood. This accumulated body of research shows that catalytic reaction of hydrocarbons with dual-zeolite function is worthy of further investigations. In this study, the cracking characteristics of C_8 paraffins on HY and HZSM-5, and on a random mixture of these zeolites have been examined.

EXPERIMENTAL

The feedstocks, *n*-octane (99.7%) and 2-methylheptane (99.8%) were obtained from Aldrich and used without further purification. Impurities present in *n*-octane were nhexane (0.2%), 2-methylheptane (0.08%) and isopentane (0.02%) while the impurities in 2-methylheptane were 3-methylheptane (0.12%) and *n*-octane (0.08%).

HY zeolite (97.3% exchanged) was prepared from NaY (Linde Lot No 45912, SK40; Si/Al = 2.4) by repeated exchange with 0.5M ammonium nitrate solution. HZSM-5 (Si/Al = 105) was provided by SNAM Progretti S.P.A. Milan, Italy. Catalysts of mesh size 80/100 were calcined at 500°C before use.

Experiments were performed on catalysts of mesh size 80/100 (~175 micron) which was diluted in a sand matrix that had been thoroughly washed with concentrated HCl and neutralized with concentrated NH_3. As the sand acted as an inert support material, it was crucial that it was catalytically inactive. For this reason, the sand matrix used was soaked in concentrated HCl for several days to remove impurities present in the sand. The liquor was replaced everyday to maintain the cleaning activity of the acid. After soaking, the sand was washed thoroughly with distilled water followed by neutralization with concentrated ammonia. Finally, the sand was filtered and rinsed with distilled water several times before it was oven dried at 500°C overnight. The activity of the sand was tested by performing the experiments in the absence of catalyst (thermal cracking).

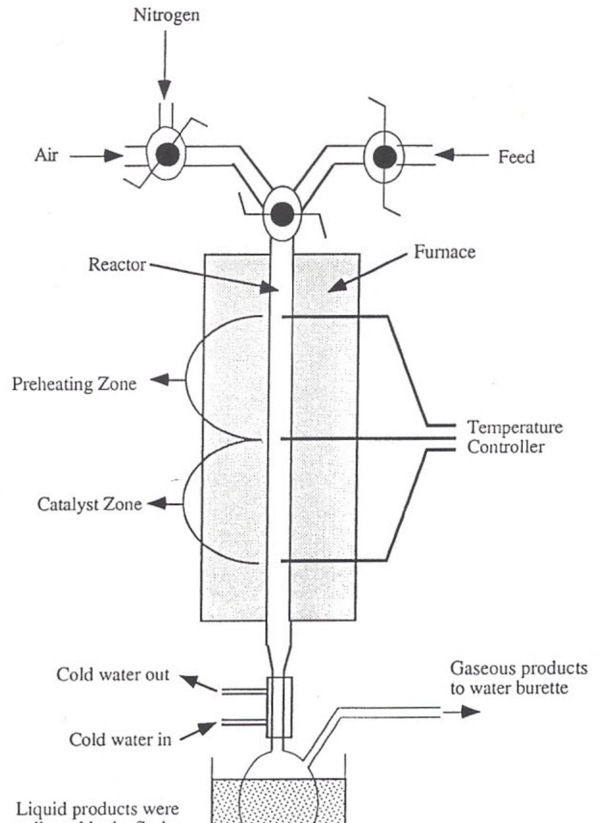


Figure 1: Experimental Apparatus

The experimental apparatus, as shown in Figure 1, consisted of a quartz reactor about 60 cm long and 2 cm i.d. The reactor was enclosed in an aluminium alloy furnace with three thermocouple probes attached to it. The reactor consisted of two zones: a preheating zone at the top section and a catalyst zone at the bottom. The preheating zone was filled with inert material, beryl saddles ($Be_3Al_2Si_6O_{18}$). The catalyst used for a particular run was placed in the catalyst zone diluted with the sand matrix. Glass wool was used to separate the zones and to hold the catalyst-sand matrix in place.

For a set of experiments, a known amount of catalyst was placed in the catalyst zone, and a known amount of feed was fed in from the top of the reactor, so that there would be a defined catalyst to feed ratio (C/F). The feed was pumped by a motor driven syringe that could be set to give different rates, resulting in different time on stream (T.O.S.), that is the time required to deliver a fixed amount of feed into the reactor.

Prior to a catalytic run, the catalyst was conditioned by purging the reactor with dry, CO_2-free nitrogen at 0.50 L/min for 5 minutes. The feed was then injected into the top end of the reactor at a constant rate by a motor driven syringe pump. The liquid products exiting the bottom end of the reactor were collected in a round bottom flask immersed in an ice bath, while the gaseous products were trapped in a 3 L gas burette by displacement of water. After the run, the reactor was once again purged with nitrogen at the same flow rate for the same period of time as before in order to flush down all remaining liquid and gases left in the reactor.

The liquid products were analysed using a Hewlett Packard 5890 II gas chromatograph with an SGE fused silica capillary column (50 m x 0.22 mm i.d.) and flame ionization detector. Gaseous products were also analysed using a Hewlett Packard gas chromatograph of the same type with a Chrompak capillary column (25 m x 0.32 mm i.d.). Data handling was facilitated using a DAPA software package. Identification of hydrocarbon products was assisted by use of a Hewlett Packard 5890 gas chromatograph coupled to a 5970 mass selective detector.

The GC temperature program for analysing the gaseous products was isothermal at 30°C for 3 minutes, followed by first ramping at 6°C/min to 60°C then at 30°C/min up to 200°C at which it was held for 8 minutes before it then cooled down to the initial temperature. The carrier gas used was a mixture of helium and nitrogen set at 27 kPa head pressure. The GC program for analysing the liquid products was isothermal at 30°C for 6 minutes, followed by first ramping at 5°C/min to 150°C and 25°C/min to 200°C at which it was held for 12 minutes, then cooling down to the initial temperature. The carrier gas used was the same as that for analysing the gaseous products, set at 165 kPa head pressure.

After a run, the catalyst became poisoned by the carbonaceous material, regarded as coke, left in its pores. This was indicated by the black appearence of the catalyst. In order to achieve catalyst regeneration, the reactor temperature was set to 500°C with dry, CO_2-free air was passing through. The gas stream coming off the bottom end of the reactor contained water vapour, CO and small amounts of CO_2 that were formed from decomposition of the coke. This gas stream then passed through a drierite absorbant, in which the water vapour was removed, then an alumina supported platinum catalyst (Pt/Al_2O_3) held at 350°C, in which the carbon monoxide was converted to carbon dioxide. The stream was finally passed through an ascarite absorbant, where all the carbon dioxide was absorbed. It was assumed that the weight increases of these absorbants provides a reliable quantitative measure of the coke produced. The duration of the catalyst regeneration varied between 1 to 3 hours depending on which and how much zeolite was used, as well as times on stream. This regeneration time was determined to be sufficient by performing duplicate runs at the same time on stream. Regeneration of HY zeolite normally took place in about 1.5 to 3 hours, and within 1 to 2 hours for HZSM-5 zeolite. With this procedure, it was possible to perform repetitive experiments with reproducible results.

RESULTS AND DISCUSSION

For individual paraffins and the mixed feedstocks, experiments were carried out over a range of times on stream, generally between 500 and 1500 seconds. It has been shown that both HY and HZSM-5 undergo ageing during cracking reactions of *n*-octane at 400 °C. Application of the time on stream theory to these systems [14] shows that for reaction of *n*-octane on HY between 75% and 95% of active sites would be poisoned with these limits of run duration. On HZSM-5 under similar conditions between 35% and 62% of active sites are poisoned. In general, the observations reported here were found to be independent of time within the experimental run durations studied, unless otherwise stated.

A. Reactions of Individual Feedstocks

Distribution of Products by Carbon Number

Results in Figures 2 and 3 compare the total product distributions from cracking of 2-methylheptane and *n*-octane on HY and HZSM-5 respectively, at similar conversion levels. Product distributions from reactions on HY show that the tendency to produce C_1 to C_3 fragments is higher for the linear paraffin. In contrast, for reactions on HZSM-5, the proportions of C_1 and C_2 cracking fragments are higher for reaction of the isoparaffin. However, patterns of overall fragmentation are similar on both catalysts (Figures 2a and 3a), showing much less variation than changing the catalyst using a particular feedstock (Figure 4). Greater variations can be seen by examination of individual distributions of paraffins, olefins and aromatics (Figures 2b-d and 3b-d).

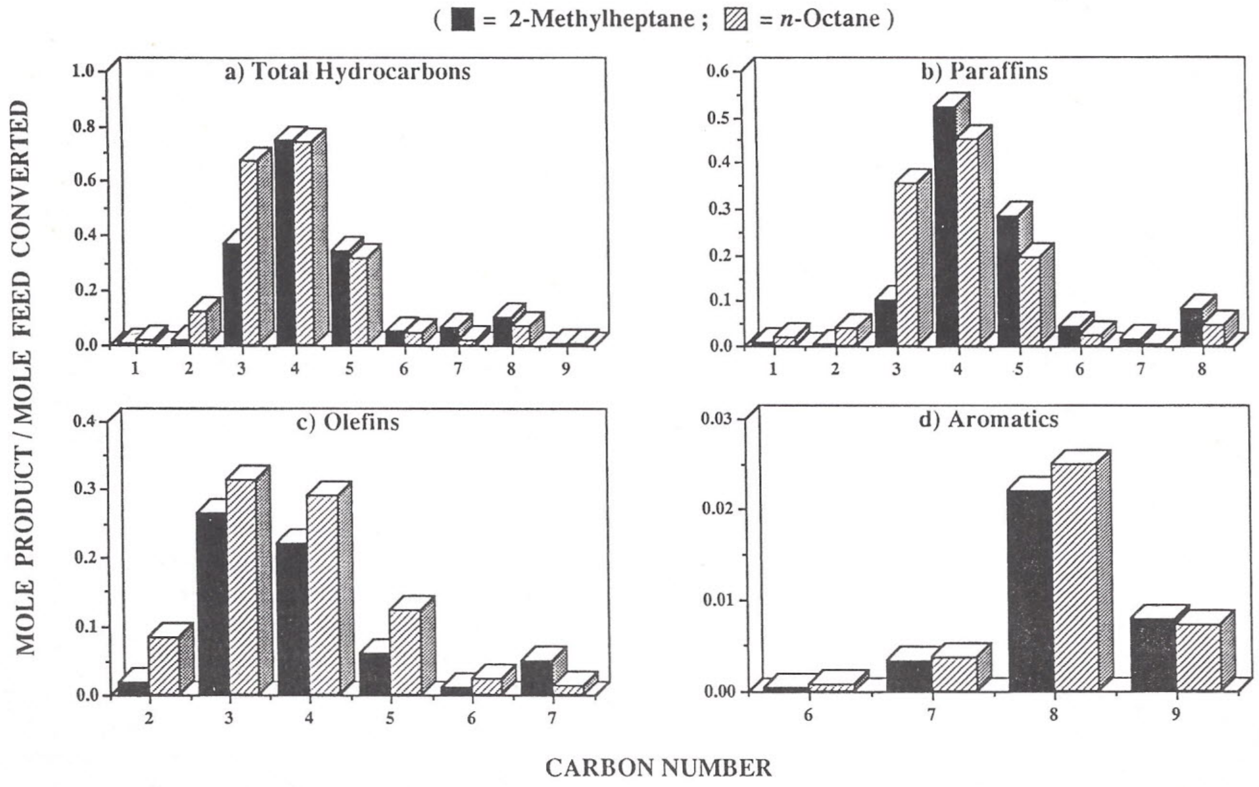


Figure 2 Product distributions from reaction of 2-methylheptane (cat/feed = 0.0620, 25.9% conversion) and *n*-octane (cat/feed = 0.0579, 17.0% conversion) on HY at 400°C

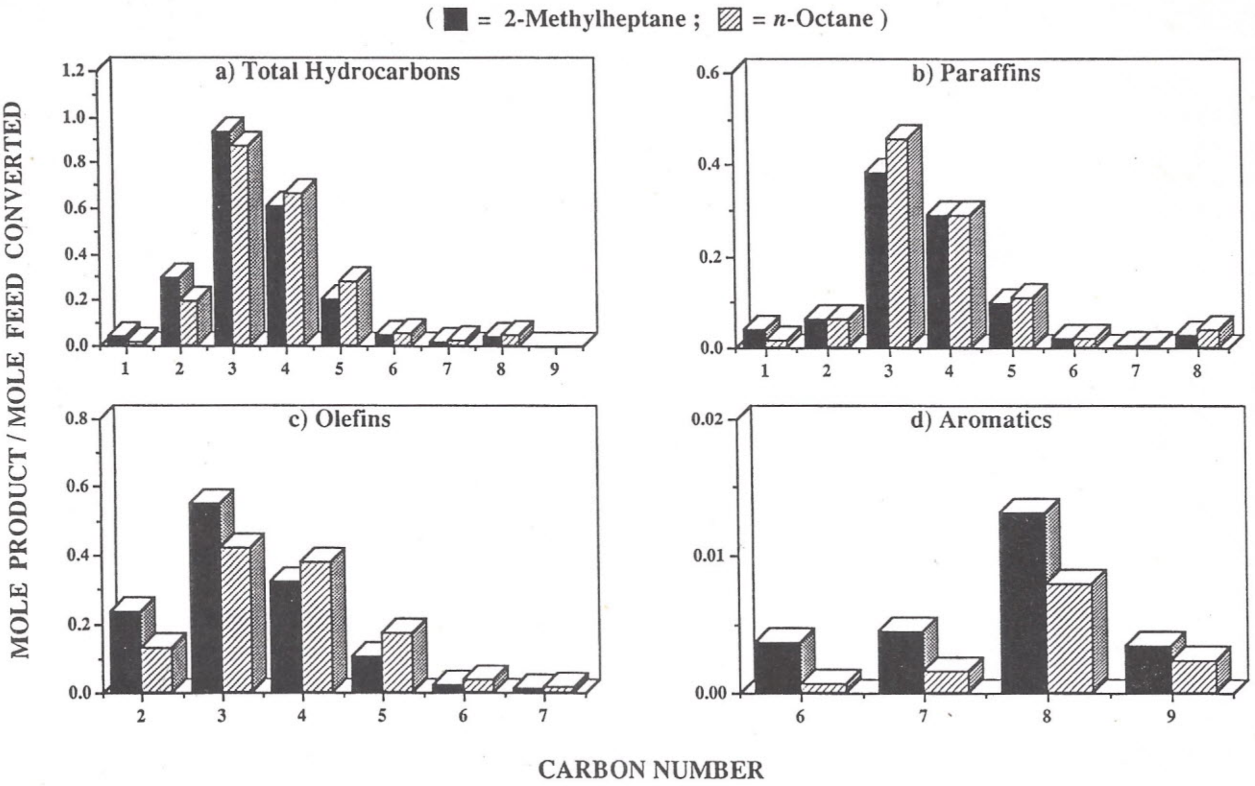


Figure 3 Product distributions from reaction of 2-methylheptane (cat/feed = 0.0416, 22.4% conversion) and n-octane (cat/feed = 0.0179, 18.0% conversion) on HZSM-5 at 400° C

As can be seen in Figure 2d, there is little difference in the total amount or distribution of aromatics produced from either paraffin feedstock on HY. It has been suggested [15] that aromatics are formed during cracking of paraffins mainly through secondary processes involving olefins. Figure 2c shows that the distribution and amounts of potential olefin precursor are similar for both feedstocks. For reaction on HZSM-5, there is a significantly higher tendency to produce aromatics from reaction of the isoparaffin (Figure 3d). For example, the amount of benzene produced is ten times greater for reaction of 2-methylheptane at similar conversion levels. However, if olefin precursors are again considered, Figure. 2c shows that amounts and distributions are similar, suggesting that, on HZSM-5 aromatic products are formed directly from the feedstock, as well as through olefins in secondary processes.

Ratios of Branched to Linear Isomers

The relative amounts of branched and linear isomers present in gasoline for both olefins and paraffins is important in determining the octane rating. A pentasil addition to an HY zeolite can influence the ratio of branched to linear (B/L) isomers produced during cracking of gas oils [3, 7, 8]. Figure 5a gives ratios of B/L isomers for C_4 and C_5 olefin products, showing the influence of both catalyst and feedstock for reaction of 2-methylheptane and n-octane. In general, higher ratios are observed for both

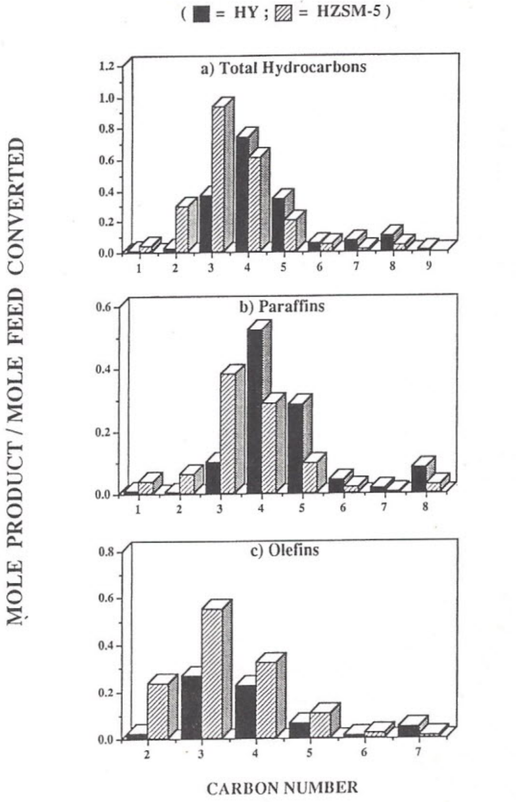
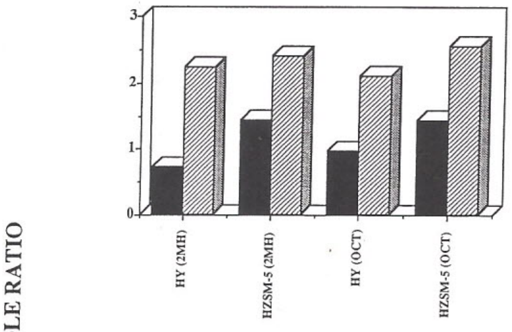


Figure 4 Product distributions from reaction of 2-methylheptane on HY (cat/feed = 0.0620, 25.9% conversion) and HZSM-5 (cat/feed = 0.0416, 22.4% conversion) at 400° C

(a) Branched to Linear Olefins (■ = C_4 ; ▨ = C_5)



(b) Branched to Linear Paraffins (■ = C_4 ; □ = C_5 ; ▨ = C_6)

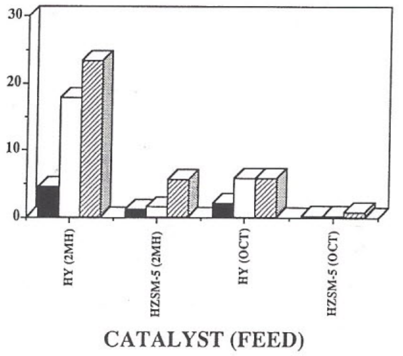


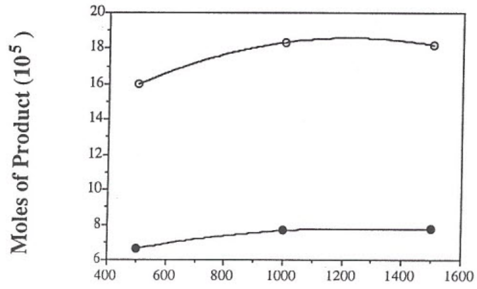
Figure 5 Ratios of B/L isomers from reaction of 2-methylheptane (2MH) and *n*-octane (OCT) on HY and HZSM-5 at 400°C
For reaction of 2-methylheptane on HY : cat/feed = 0.0620, 25.9% conversion
on HZSM-5 : cat/feed = 0.0416, 22.4% conversion
For reaction of *n*-octane on HY : cat/feed = 0.0579, 17.0% conversion
on HZSM-5 : cat/feed = 0.0179, 18.0% conversion

C_4 and C_5 olefins for reactions of either feedstock on the pentasil. The effect of changing either the catalyst or the feed on the ratios of B/L olefins is more noticeable for the C_4 species.

Variations in the ratios of B/L paraffin products are much more significant than observed above for the olefins (Figure 5b). In contrast to the olefinic products, both catalyst and feedstock exert a major influence on the observed degree of branching of the saturated cracking fragments. For both feedstocks, the ratios of B/L paraffin products is significantly higher for reaction on HY compared to HZSM-5. This effect is seen particularly for the C_5 paraffins, where, for both feedstocks the observed B/L ratios are 12 - 24 times higher on the faujasite. Figure 5b also shows that, for either catalyst the ratios of B/L saturated isomers are significantly higher for cracking of the branched feedstock. This result shows that the intermediates formed are not identical for cracking of the linear and branched C_8 paraffins. The dominant cracking pathway on either catalyst cannot result from equilibrium of the various possible branched and linear C_8 carbonium ions as previously suggested [16].

Branched C_6 paraffins can result from cracking of 2-methylheptane by direct cleavage of a C-C bond which would produce exclusively 2-methylpentane. Alternatively, bimolecular processes leading to a C_6 carbenium ion after ß-scission could give rise to either 2-methylpentane or 3-methylpentane after rearrangement of the residual C_6 carbenium ion. Rearrangement of a C_6 carbenium ion to give branched isomers occurs on both HY and HZSM-5 to produce similar product distributions [17, 18]. For skeletal isomerization of linear hexenes, the ratios of 2-methylpentenes to 3-methylpentenes formed were 0.76 and 0.62 on HY and HZSM-5 respectively [17, 18]. Figure 6 shows a marked preference for formation of 2-methylpentane rather than 3-methylpentane for cracking of 2-methylheptane on both HY and HZSM-5. The ratios of the C_6 isomers formed suggest that on both catalysts, direct cracking via protolysis is favoured over processes involving an intermediate C_6 carbenium ion. Results obtained over a range of times on stream as illustrated in Figure 6 show that the reported phenomena are not strongly influenced by catalyst decay.

(a) 2-Methylpentane (○) and 3-Methylpentane (●) on HY



(b) 2-Methylpentane (□) and 3-Methylpentane (■) on HZSM-5

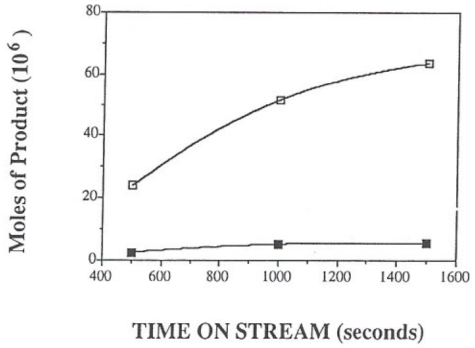


Figure 6 Formation of 2-methylpentane and 3-methylpentane from reaction of 2-methylheptane on HY (cat/feed = 0.0620, 25.9% conversion) and HZSM-5 (cat/feed = 0.0416, 22.4% conversion) at 400°C

Reaction on a Random Mixture of HY and HZSM-5

Product distributions for reactions of n-octane and 2-methylheptane respectively on a random mixture of HY and HZSM-5 are shown in Figures 7 and 8. Calculated distributions are also presented, using the product distributions for reactions on the individual catalysts, assuming that the relative contribution is proportional to activities on the isolated zeolite. Although the overall distributions on the random mixture of HY and HZSM-5 are well represented by the calculated values (Figures 7a and 8a), greater deviations are seen considering the observed and predicted distributions for individual product classes. These deviations can be attributed to additional processes where products formed on one catalyst interact with the second catalyst, particularly in secondary processes involving

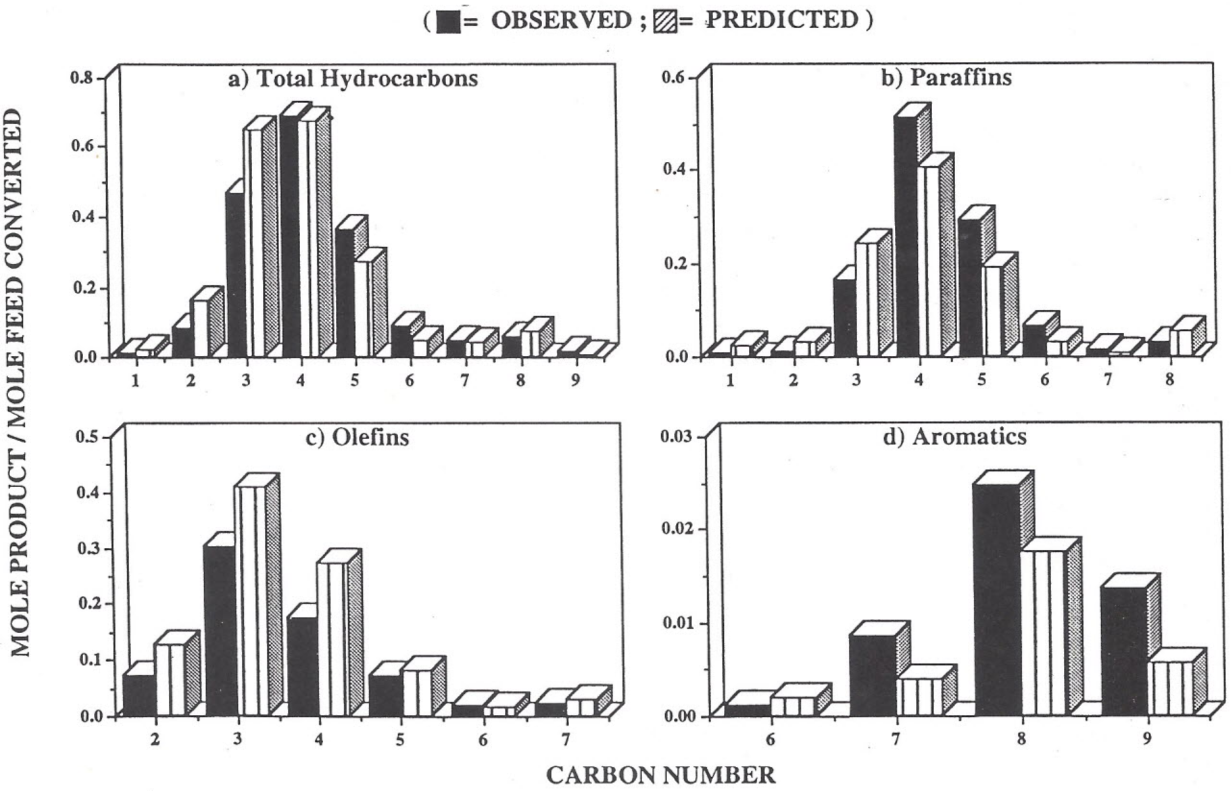


Figure 7 Product distributions from reaction of 2-methylheptane on a random mixture of HY and HZSM-5 (HY/HZSM-5 = 1 : 0.67, 34.6% conversion) at 400°C

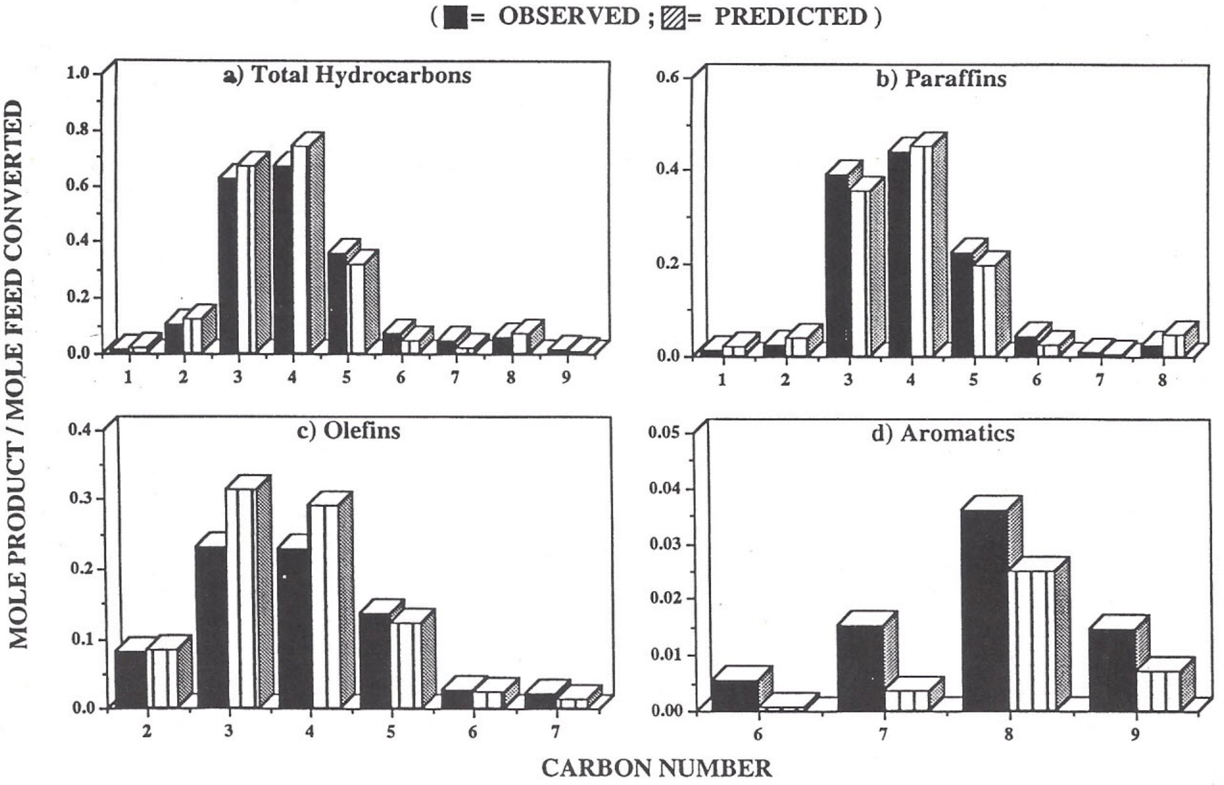


Figure 8 Product distributions from reaction of n-octane on a random mixture of HY and HZSM-5 (HY/HZSM-5 = 1 : 0.31, 32.1% conversion) at 400°C

hydrogen transfer and isomerization. Figure 9 shows a comparison between observed and predicted B/L ratios for both olefins and paraffins. Although observed ratios for the olefins are close to predicted values, addition of HZSM-5 to the HY zeolite leads to a cracking product distribution with a somewhat higher degree of branching of the product olefins. Predicted ratios for the C_4 - C_6 paraffins show greater deviation from the observed values (Figure 9b) with more branching observed than expected for reaction of the branched isomers, while the reverse is true for reaction of the linear C_8 paraffin.

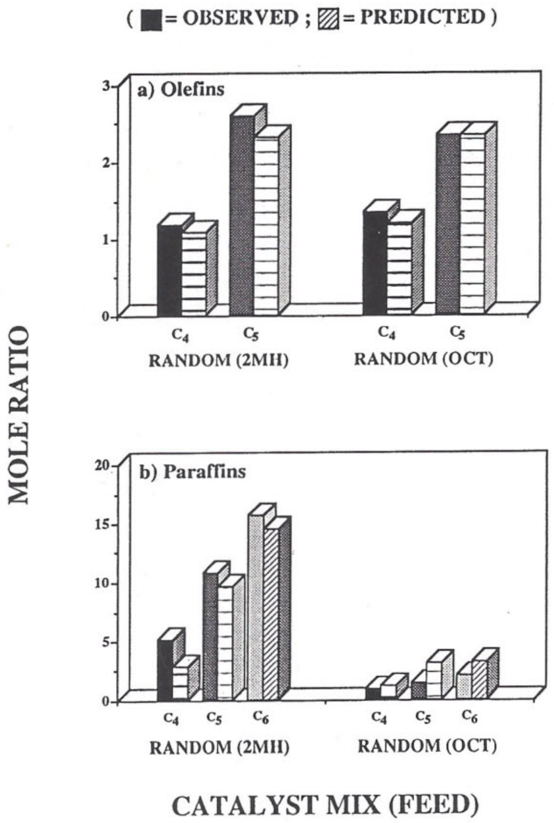


Figure 9 Ratios of B/L isomers from reaction of 2-methylheptane (2MH) and *n*-octane (OCT) on a random mixture of HY and HZSM-5 at 400°C
For reaction of 2-methylheptane: HY/HZSM-5 = 1:0.67, 34,6% conversion
For reaction of *n*-octane: HY/HZSM-5 = 1 : 0.31, 32.1% conversion

B. Reactions of Mixed Feedstocks

The relative rates of conversion of C_8 isomers in a mixed feedstock (1 : 1 molar ratio), shown in Figure 10, agree with those of Chen and Garwood [19]. A random mixture of the catalysts produces preferential cracking of the linear isomer, in agreement with previous studies [2] on complex feedstocks. Figure 11 shows a comparison of product distributions from cracking the paraffin mixture shifted to lower molecular size on the pentasil. Ratios of B/L paraffin isomers are significantly higher for reaction on HY compared to HZSM-5 (Figure 12). In contrast, the corresponding ratios for C_4 and C_5 olefins are increased by the pentasil. Both effects were previously observed for reaction of the individual feedstocks. Figure 12 also shows observed ratios for olefinic products corresponding closely to calculated values, with ratios for paraffins significantly higher than calculated.

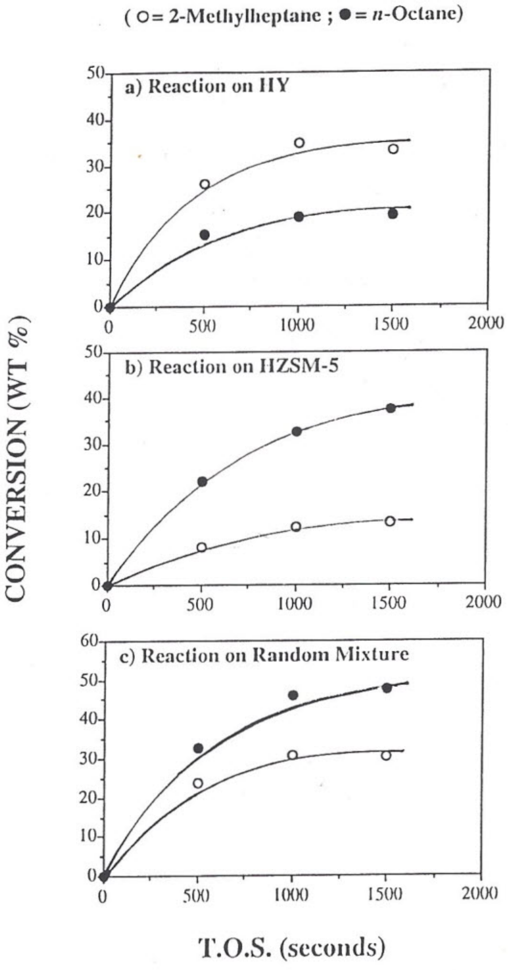


Figure 10 Conversion of 2-methylheptane and *n*-octane in a mixed feed from reaction on HY, HZSM-5 and a random mixture of the catalysts at 400°C

Product distributions from reaction of the C_8 paraffin mixture on a random mixture of the zeolites is given in Figure 13. As for reactions on the individual catalysts, the distribution of total cracking products is well represented by the predicted distribution. The B/L ratios for C_4 olefins (Figure 14a) lie between those for reaction on the individual catalysts whereas for C_5 olefins this ratio is higher than cracking on either HY or HZSM-5 (Figure 12a). Production of the branched isomers is higher than predicted. Figure 14b shows that the ratios for paraffins lie between those obtained on the individual catalysts (Figure 12b), but are somewhat lower than predicted.

Cracking of a mixture of paraffins on a random mixture of zeolites can be considered in the context of reported studies for cracking of complex gas oil mixtures concerning the impact of addition of HZSM-5 to a Y zeolite. It has

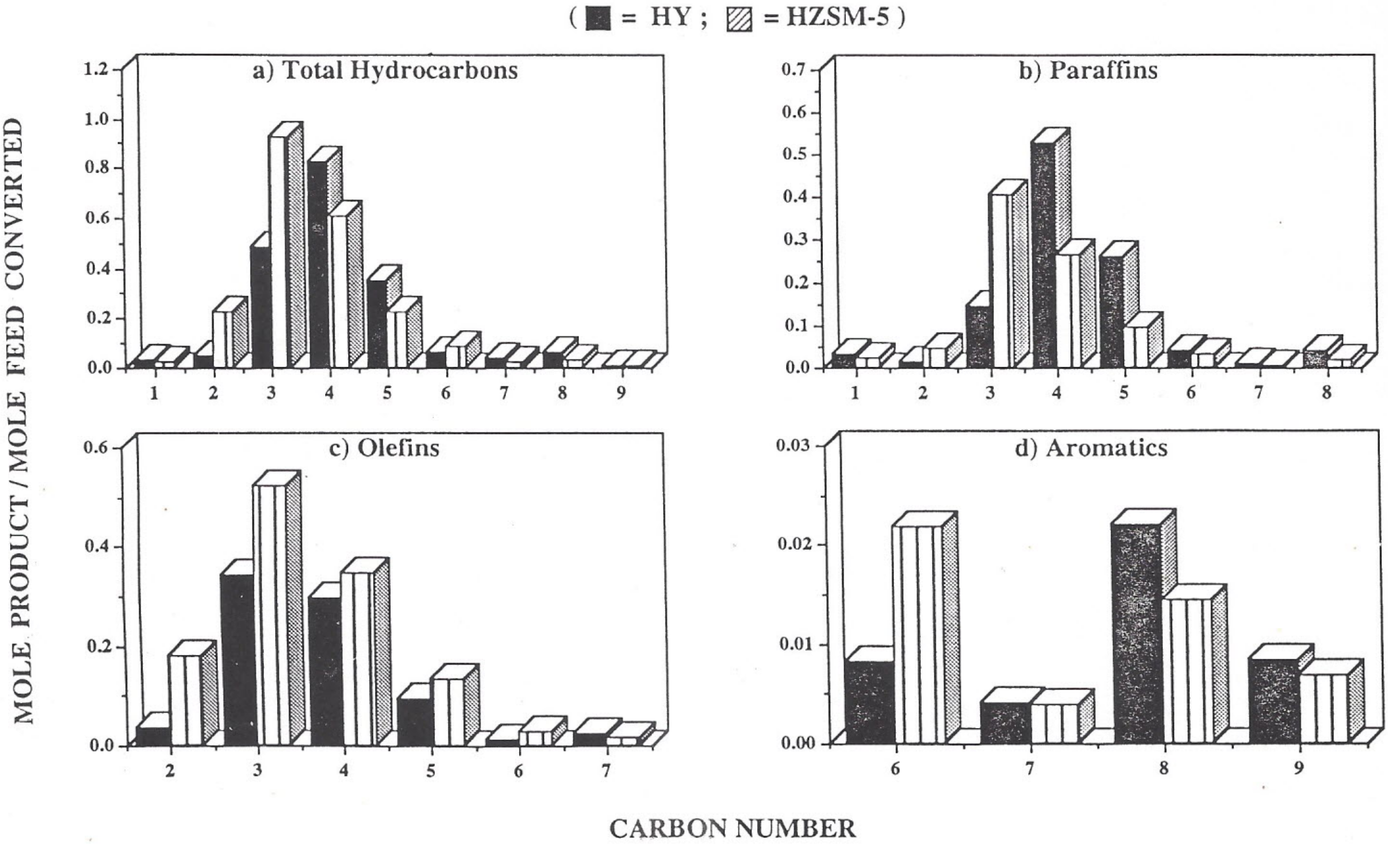
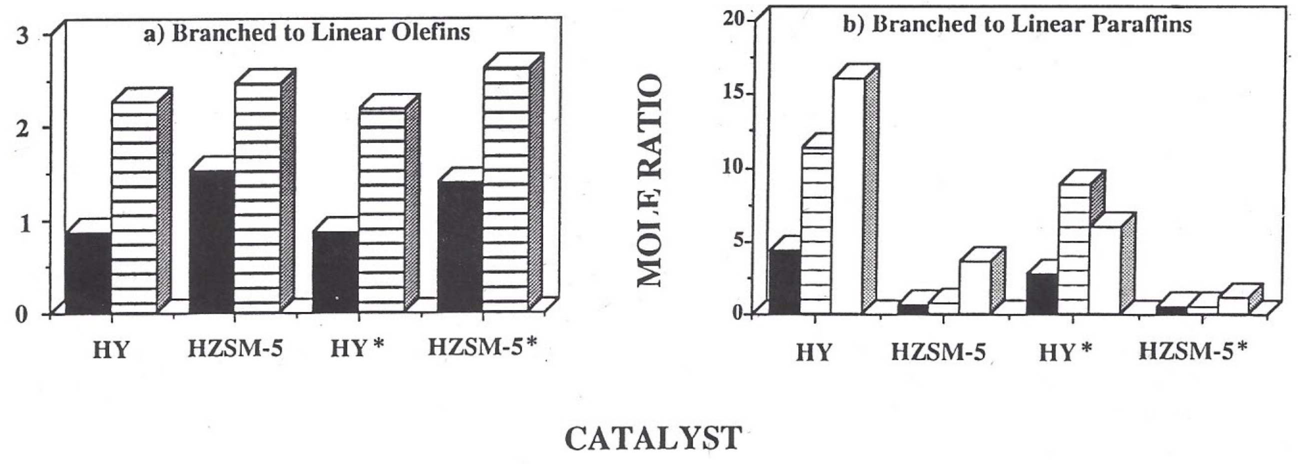


Figure 11 Product distributions from reaction of a mixture of 2-methylheptane and n-octane on HY and HZSM-5 at 400 °C (TOS = 1000 seconds)



(a) Branched to Linear Olefins (■ = C_4 ; ▨ = C_5)

(b) Branched to Linear Paraffins

(■ = C_4 ; □ = C_5 ; ▨ = C_6)

Figure 12 Ratios of B/L isomers from reaction of a mixture of 2-methylheptane and n-octane on HY and HZSM-5 at 400 °C (TOS = 1000 seconds)
Calculated values are denoted by asterix (*)

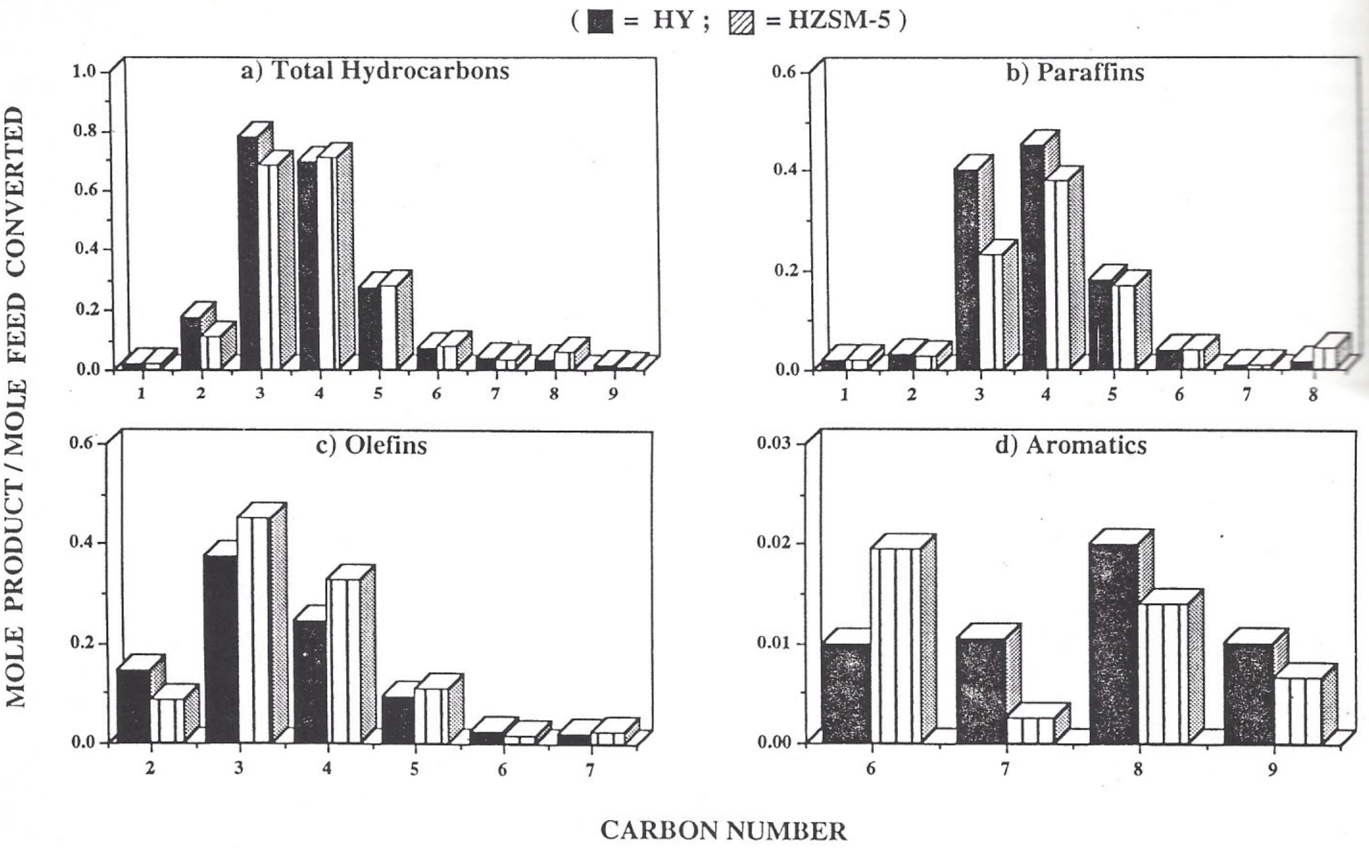
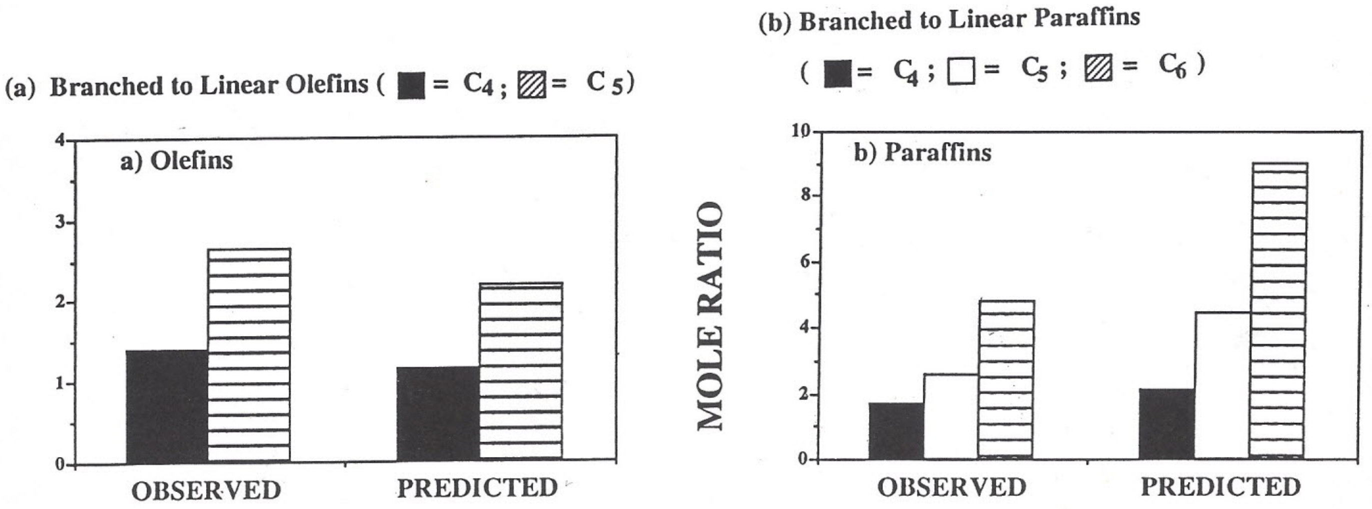


Figure 13 Product distributions from reaction of a mixture of 2-methylheptane and *n*-octane on a random mixture of HY and HZSM-5 at 400°C (TOS = 1000 seconds)


(a) Branched to Linear Olefins (■ = C_4 ; ▨ = C_5)

(b) Branched to Linear Paraffins (■ = C_4 ; □ = C_5 ; ▨ = C_6)

Figure 14 Ratios of B/L isomers from reaction of a mixture of 2-methylheptane and *n*-octane on a random mixture of HY and HZSM-5 at 400°C (TOS = 1000 seconds) been suggested that pentasil addition produces selective removal of low octane linear paraffins, and can contribute towards enhancement of gasoline quality. However, the present studies consistently show that cracking of either linear or branched paraffins results in a greater proportion of linear paraffin isomers at lower molecular weight. In contrast, reported cracking studies on gas oils indicate higher B/L ratios of C_4 and C_5 paraffins on pentasil addition [3, 6, 8]. This suggests that enhanced selective cracking of linear paraffin isomers by HZSM-5 is not the dominant mechanism for octane rating enhancement. Higher ratios for B/L isomers of light olefins have also been reported for studies on gas oils [2, 5, 6], in agreement with the present studies. The presence of HZSM-5, however, contributes to the isomerization of olefins, increasing the proportion of branched isomers, thereby enhancing the octane rating of the gasoline produced.

CONCLUSION

This present study shows that both catalyst and feedstock are important factors in determining product distribution for cracking of paraffins, particularly on ratios of branched to linear paraffins produced. Preferential cracking of linear paraffins rather than branched isomers in a complex mixture by introduction of a pentasil additive may be expected to result in enrichment of the linear saturates at lower carbon number. As this has not been generally observed for gas-oil cracking, selective cracking of linear paraffins by the pentasil additive may not be the dominant mechanism leading to octane enhancement of the gasoline produced.

ACKNOWLEDGEMENT

The author is indebted to the Research and Development Centre for Applied Chemistry of the Indonesian Institute of Sciences for the financial support.

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