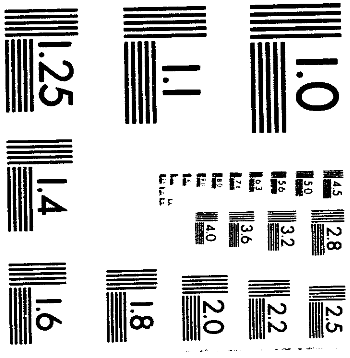
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NIPER-658
September 1993

TOPICAL REPORT

RELATING FEEDSTOCK COMPOSITION to PRODUCT SLATE and COMPOSITION in CATALYTIC CRACKING:

1. BENCH SCALE EXPERIMENTS with LIQUID CHROMATOGRAPHIC FRACTIONS from WILMINGTON, CA, >650° F RESID.

by

J. B. Green, E. J. Zagula, J. W. Reynolds,

H. H. Wandke, L. L. Young, and H. Chew

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National Institute for Petroleum and Energy Research
P. O. Box 2128
Bartlesville, OK 74005
(918)-336-2400

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ABSTRACT

The catalytic cracking behavior of compound types in the >650° F resid from a Wilmington, CA, 14.2° API crude was investigated. Liquid Chromatography (LC) was used to separate the resid into eight fractions. These fractions were used as feedstocks for a bench scale fluidized catalytic cracking (FCC) unit.

Gasoline was produced almost exclusively from neutral (65 % of whole resid) components. Acidic and basic types were partially converted to coke plus small amounts of C_1 and C_2 gases, with the balance primarily carrying over as heavy liquid products. Gasoline composition depended on the type and quantity of polar compounds present in the feed because both acidic and basic compounds inhibited cracking reactions (β-scission, hydrogen transfer, etc.) to varying degrees. In accordance with prior work, basic nitrogen compounds exhibited the largest inhibitory effect on cracking. Their effect is dependent on concentrations up to a limiting value which may correspond to saturation of susceptible catalyst sites. On an equal weight basis, the effect of high boiling (high molecular weight) bases was less than those occurring in the 650-1000° F distillate range. Partitioning of nitrogen present in acidic (e.g. carbazole) forms in the feed into liquid products was greater than for basic nitrogen. Thiophenic forms of sulfur partitioned more into liquid and less into gaseous (H_2S) products than sulfide-type sulfur. Coke yield was approximately proportional to microcarbon residue test results for all feeds. Ongoing work with additional feedstocks has indicated behavior similar to that of Wilmington. Selected Wilmington liquid products are undergoing detailed analysis in order to determine relationships between feed versus product composition, particularly with respect to acidic and basic types.

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INTRODUCTION

Fluid Catalytic Cracking (FCC) is a major refining process for production of light distillates from petroleum heavy ends. Its history and economic importance have been highlighted in several articles.[1-4] Because of the compositional complexity of gas oils and other petroleum fractions used as feedstocks, and the complexity of the cracking reactions themselves, the relationships between feedstock versus product composition under a given set of cracking conditions may be expressed only in general terms and parameters.[5-7] For example, metals, basic nitrogen and carbon residue are negative attributes of a given feedstock, whereas increases in H/C ratio and saturate/monoaromatic content, or decreases in molecular weight/boiling point in feeds result in increased yields of light products.

Existing models for predicting FCC product slate are generally based on the distribution of hydrocarbon types in the feed. For example, Jacob et al. incorporated the proportions of paraffinic molecules, naphthenic molecules, carbon in aromatic rings and carbon in aromatic substitutents into a lumped kinetic model which is valid for a wide range of conventional feeds and process conditions.[8] The decreased catalytic activity from poisoning by basic nitrogen up to levels of 0.1 wt% was also incorporated into their model.

Because of the susceptibility of the catalyst to reversible poisoning by basic nitrogen and coke, and irreversible poisoning by metals, raw atmospheric resids and heavy distillates from most heavy oils and syncrudes are not suitable as feedstocks for current FCC units.[9] In addition, the large quantity of coke formed from cracking many of these low grade feedstocks would overload the catalyst regenerator and raise emissions of sulfur oxides released during regeneration to unacceptably high levels. Therefore, extensive pretreatment of these materials prior to FCC and/or modifications(s) of the FCC process itself will be required before cracking could be considered as an economically or technically viable option for very low grade feedstocks. With regard to feed pretreatment, "sledge hammer" techniques could be used, such as coking, with the corresponding low liquid and high coke yields associated with this type of approach. Alternately, selective removal of components most detrimental to cracking could be attempted in order to provide the highest liquid yield within economic constraints. A limitation toward pursuing the latter option is that the cracking behavior of many of the compound classes abundant in low grade feedstocks is not known - - at least beyond the degree of understanding afforded by inspection analyses. Existing FCC models do not directly address the effects of high molecular weight polar compound types because of their negligible concentration in conventional FCC feeds.

The objective of this work was to determine the cracking behavior of major compound classes in atmospheric resids from heavy oils. This information will be used to assess feasibility of selective pretreatment of low grade feedstocks prior to catalytic cracking. It should also provide greater insight into the effects of polar compound classes on cracking than is currently available. For example, much of the current information on basic nitrogen poisoning is based on behavior of pure compounds or simple inspection analyses.[10-14]

Liquid chromatographic (LC) separation methods were used to fractionate resids into compound classes, which were cracked using a bench scale FCC unit. Cracking behavior was assessed from the resulting product slate and the composition of gaseous and liquid products obtained. This report discusses results obtained from the initial resid investigated. It was obtained from a Wilmington, CA, 14.2° API gravity crude. The Wilmington crude was chosen because it is one of the most extensively characterized petroleums available, and also because it contains high levels of both N and Ni.[15-29] The Wilmington >1000° F resid was employed in a prior study of coking tendencies of compound classes in vacuum resids,[30] and the gas oil (650-1000° F) was utilized in an earlier catalytic cracking study.[31]

EXPERIMENTAL

Feedstock Preparation

Figure 1 shows the overall scheme for feedstock preparation. The 650-1000° F and >1000° F boiling ranges were obtained from the whole crude via thin-film distillation using apparatus and procedures described elsewhere.[32] Methodology for nonaqueous ion exchange LC separation of acid, base and neutral types from each boiling range has also been described in prior reports.[25,32] Removal of sulfides and small amounts of polar compounds carrying over into the neutral fraction was accomplished via percolation of whole neutrals through silica (polars) and Pd(II) ligand exchange (sulfides) LC columns connected in series using prescribed procedures.[33]

The effect of sulfides/polar-neutrals on cracking behavior of neutrals was assessed from comparison of runs of whole neutrals versus sulfide/polar-free neutrals. Cracking behavior of acid and base fractions was assessed from comparison of runs of whole neutrals versus blends of

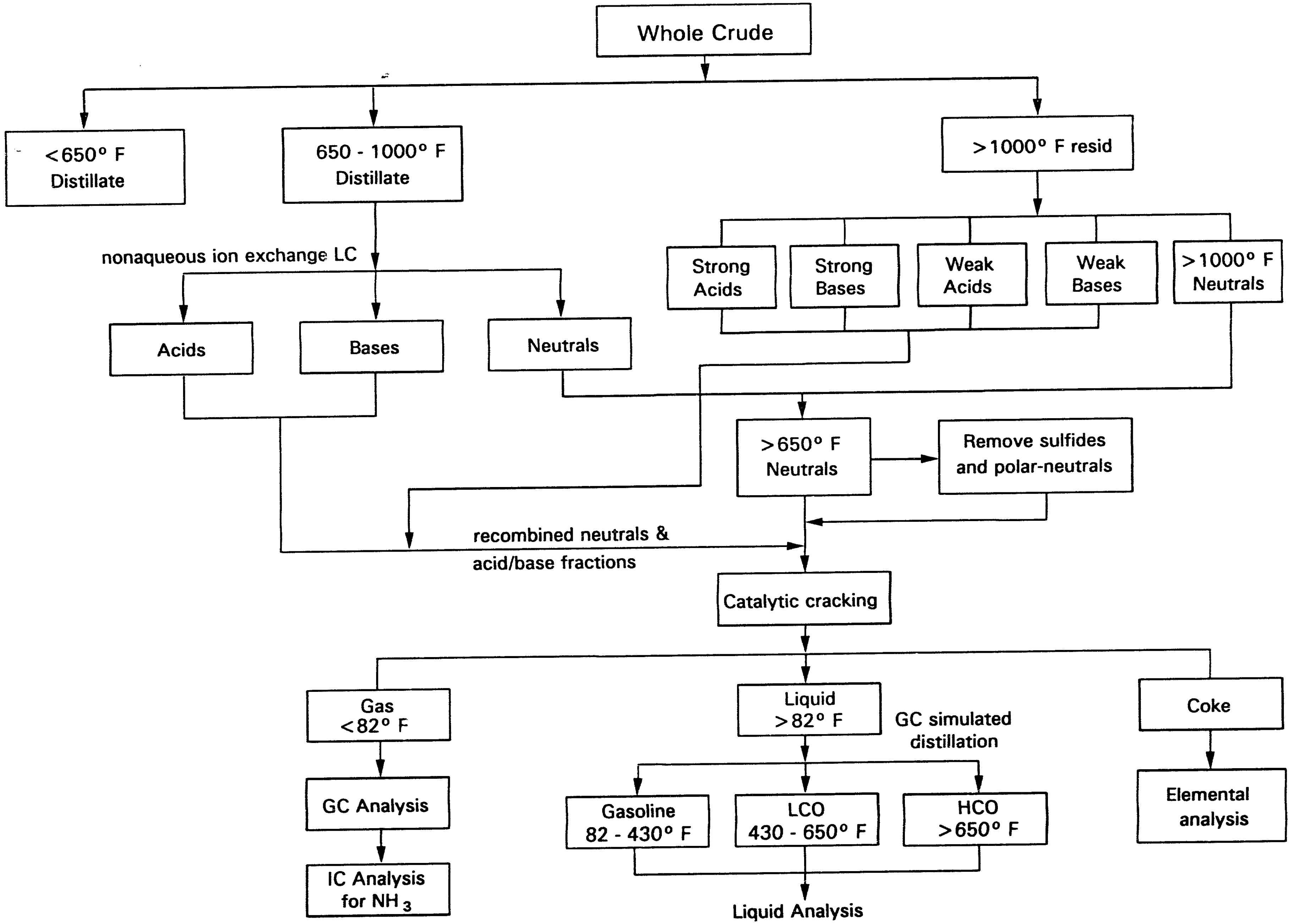


Figure 1. Scheme for LC fraction blending and catalytic cracking.

acids/bases plus neutrals. Blending of acid and base fractions with neutrals prior to cracking was a practical necessity because of their intractable physical properties (typically brittle solids at room temperature). Also, cracking of neat acid or base fractions would have been very far removed from any practical refining situation. Blending of fractions was accomplished with stirring and heat. Selected blends were checked for incomplete mixing via hot filtration. Negligible insolubles were observed in each case. Microcarbon residue (MCR) was determined on LC fractions and blends via ASTM D 4530.

Catalytic Cracking

The microconfined bed unit (MCBU) employed for the cracking experiments was developed at Phillips Petroleum Co. Its operation and applications in catalytic cracking research have been described in several reports and papers.[11,34-38] The overall apparatus is illustrated in figure 2.

For this work, the liquid collection traps were modified to improve efficiency and an all-Teflon gas sampling train was installed to prevent losses of H_2S and (potentially) NH_3 on metal surfaces. The initial liquid trap (No. 1) was fabricated from the following components (Kontes, Vineland, NJ): glass coil (cat. 994204-040), 5 mL centrifuge tube (cat. 410500-0005), and 12/5 balljoints with O-ring seal (cats. 671300-0125 and 671500-0125). The overall 28 cm length of the trap was attained by joining a piece of glass tubing onto the top of the centrifuge tube. During operation, the total product vapor passed through the cooling coil and entered the body of the trap near the top of the centrifuge tube. Uncondensed materials exited the top of the trap and entered trap number two. This trap consisted of a gas impinger (Ace Glass, Vineland, NJ, cat. 7530-11) fitted with 12/5 O-ring seal ball joints. It was loosely packed with glass wool to remove entrained mist in the vapor phase. The gas collection system downstream of the liquid traps was assembled from Teflon tubing and appropriate fittings (Fluoroware Inc., Chaska, MN). The gas itself was collected in a Tedlar bag with approximate dimensions (flat) of 41 x 33 cm. Gas volume was determined by water displacement, as noted in figure 2. The water bath containing the bag was kept at 45° C to prevent condensation of C_6+-hydrocarbons present at low levels in most gas samples. A new Tedlar bag was used for each run; each bag was evacuated prior to use.

Because of the significant viscosity of most of the feedstocks, they were heated prior to and during injection. The 20 mL size syringe typically used for sample injection was mechanically driven (Sage Instruments, Cambridge, MA) to avoid contact with the hot (100° C) syringe surfaces and to provide a uniform feed rate.

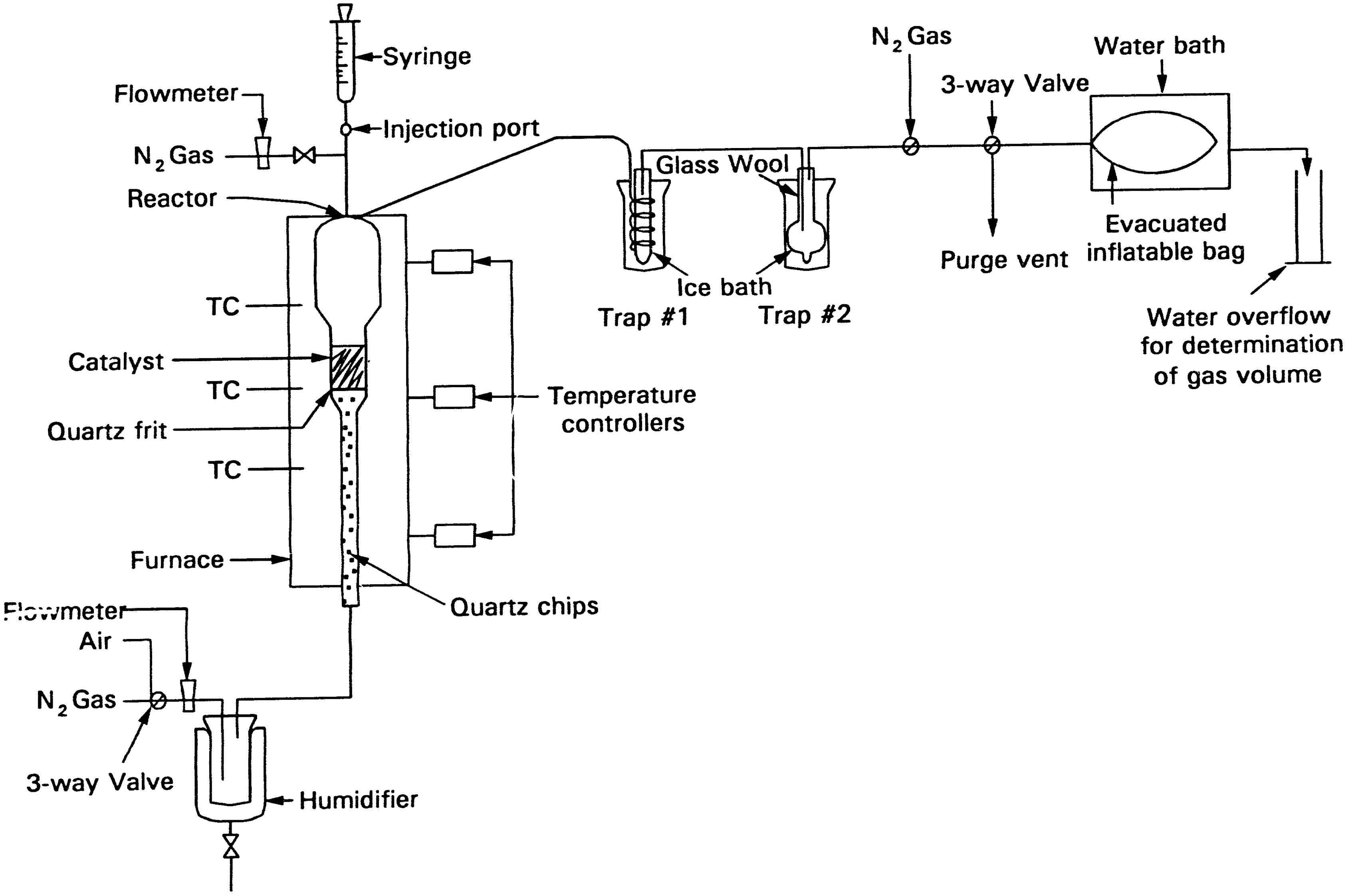


Figure 2. Microconfined Bed Unit Schematic (TC = thermocouple)

A commercial Zeolite-based equilibrium catalyst obtained from a modern refinery was used. It was ground and sieved (200-325 mesh) prior to use. Dry ice was mixed with the catalyst during screening to avoid build-up of static charges on the sieve surface. This catalyst is identical to that employed in earlier work.[37-38] Because of the significant metal content of many of the feedstocks employed, a new aliquot of catalyst (ca. 35 g) was used for each run. Each aliquot of as-received catalyst was charged to the MCBU, and coke on the as-received catalyst was burned off under air fluidization at 685° C for 22 min. The catalyst charge was computed from the difference in mass between the empty MCBU and the cooled MCBU containing the regenerated catalyst.

The reactor containing the catalyst was preheated to 521 ± 1° C(970° F) prior to each run. During the preheating period, (water-saturated) nitrogen gas flow through the bottom of the MCBU was 140 mL/min, while dry nitrogen flow through the top was 90 mL/min. Gas was vented through the exit tube of the reactor to a hood during temperature equilibration. After temperature had been reached, the liquid and gas sampling train was connected to the MCBU and the nitrogen gas was vented through a purge vent installed prior to the gas collection bag. Within 10-15 sec after connection of the sampling train, feedstock injection commenced. The feedstock was injected at a point about 2 cm above the fluidized catalyst bed through a needle fabricated from 1/8 in od stainless steel tubing. Concurrent with the start of feed injection, the purge vent was closed and the purge gas was directed to the gas sample bag. Injection of the feed (near 4.1 g - depending on the exact weight required to obtain a 8.5 cat/oil ratio) took place over 30 sec. Flow of nitrogen (140 mL/min through bottom, 90 mL/min through top) was continued for an additional 4.5 min after completion of feed injection. After 5.0 min after the start of the run (0.5 + 4.5 min), power to the reactor furnace was cut off and the furnace (Thermcraft, Winston-Salem, NC) was removed from around the MCBU. Nitrogen flow was continued thorough the complete system for an additional 1-1.5 min during cool-down, after which flow through the reactor was ceased.

After completion of the run, an additional 2,000 mL of nitrogen was typically added to the bag at a point after the liquid traps (see figure 2) to dilute the concentration of gaseous products to a range more amenable to GC analysis. A Carle (EG&G Chandler Engr., Tulsa, OK) Series 400 AGC GC configured with multiple columns, valves, thermal conductivity and flame ionization detectors, and dual valve injectors was used to analyze the composite gas sample in duplicate. Initially, portions of the gas were also analyzed for ammonia via absorption into dilute aqueous sulfuric acid followed by ion chromatography. This practice was discontinued because levels of ammonia determined were below one ppm (v/v) in all cases. Liquid products were also analyzed for ammonium sulfide in earlier cracking runs. This analysis was similarly discontinued owing to the negligible quantities found.

Product Analysis

The composite liquid was subjected to the following analyses: boiling point distribution via GC (ASTM D 2887), C and H content (via a Perkin-Elmer 240 elemental analyzer), N (chemiluminescence, D 4629) and S (microcoulometry, D 3120). These same techniques were used to determine elemental composition of feedstocks. Catalyst samples were analyzed for C, H, and N as above; S was determined via D 1552/IR.

Gasoline range components in selected whole liquid products were determined by GC/MS. A 100 m x 0.25 mm, 0.5 µm film thickness methylsilicone fused silica column was programmed at 2° C/min from 25 to 300° C for the analysis. Peak identifications were based both on GC retention index and mass spectral matching with literature data. After GC/MS analysis, the whole liquid products were separated into acid, base and neutral types via nonaqueous ion exchange chromatography. Aliquots of the acid and base fractions were analyzed by chemical derivatization/GC/MS analysis, techniques.[39-41]

RESULTS

Table I shows the distribution of compound types determined by LC separations of the Wilmington 650-1000° F distillate and >1000° F resid. Those data were used to compute the composition of the >650° F resid indicated in the table.

Table II lists the elemental composition and MCR of the Wilmington fractions. These data were used to calculate the composition of feedstocks, shown in table III. Feedstock composition provides the basis for calculation of mass balances and partitioning of nitrogen and sulfur over the cracked products. The concentrations of nitrogen, oxygen (by difference), and MCR in the feedstocks containing acids or bases are appreciably higher than that of the pure neutrals because of the high degree of enrichment of those elements in polar (acid/base) fractions (table II). The concentration of sulfur is relatively constant throughout all Wilmington feedstocks except the polar/sulfide-free neutrals, which exhibits a significantly lower sulfur content due to removal of sulfides via LC. As indicated in table III, the 650-1000° F acid and base fractions were blended with a conventional gas oil (NIPER sample number 2034) in

Table I. - Compound-type Distribution in Wilmington as a Function of Boiling Range (wt%)[a]

Sample No.	1693	1694	1693/94
Boiling Range, ° F	650-1000	>1000	>650[b]
Acids			
strong	-	11.2	7.4[d]
weak	-	15.5	10.2[d]
total	10.7 ± 0.5[c]	26.7	21.2[e]
Bases			
strong	-	11.7 ± 0.3	7.7[d]
weak	-	9.4 ± 0.1	6.2[d]
total	4.4 ± 0.1	21.1 ± 0.4	15.4[e]
Neutrals			
polar-neutral	2.1 ± 0.1	10.7 ± 0.7	7.7
sulfide	7.3 ± 0.2	10.7 ± 1.0	9.5
nonsulfide	77.3 ± 0.2	33.2 ± 1.3	48.3
total	86.7 ± 0.5	54.6 ± 2.0	65.5
Total	101.8	102.4	102.1

[a] From LC mass balances.

[b] Calculated from data for 650-1000° (34.3 wt% of >650° F) and >1000° F (65.7 wt% of >650° F) boiling ranges.

[c] Uncertainties given are average deviations from duplicate separations.

[d] Includes >1000° F portion only.

[e] Total >650° F acids or bases.

Table II. - MCR and Elemental Data for Wilmington Fractions (wt%)

Boiling Range, °F	Fraction	C	H	N	S	O (diff.)	MCR
650-1000	whole distillate	86.23	11.23	0.56	1.97	0.01	0.27
	acids	81.85	9.33	2.14	1.23	5.45	4.80
	bases	83.80	9.90	3.90	1.20	1.20	1.82
	neutrals	85.71	11.55	0.19	2.40	0.15	0.20
	polar/sulfide-free neutrals	86.90	11.34	0.15	1.40	0.21	-
>1000	whole resid	84.40	10.23	1.30	2.66	1.41	20.0
	strong acids	80.06	8.62	1.16	2.36	7.80	25.6
	weak acids	83.94	9.27	1.60	2.18	3.01	33.9
	strong bases	79.24	9.04	2.97	3.05	5.70	37.1
	weak bases	79.22	10.10	2.20	3.32	5.16	22.4
	neutrals	85.62	11.28	0.58	2.80	-	11.8
	polar/sulfide-free neutrals	85.69	10.92	0.49	1.53	1.37	-

Table III. - Wilmington Feedstock Characteristics and Composition

						Elemental Compositon of Blend, wt%					
Blend No.	Code	Component A	Wt% in Blend	Component B	Wt% in Blend	C	H	N	S	O (diff)	MCR, wt%
1	2034GO	2034 gas oil[a]	100	-	-	86.47	12.31	0.16	0.62	0.44	0.20
2	2034 + DA	2034 gas oil	89.74	650-1000° F acids	10.26	85.99	12.00	0.36	0.68	0.97	0.67
3	2034 + DB	2034 gas oil	89.74	650-1000° F bases	10.26	86.20	12.06	0.54	0.68	0.52	0.37
4	W	whole >650° F resid	100	-	-	85.03	10.57	1.05	2.42	0.93	13.4
5	W + SA	whole >650° F resid	84.37	>1000° F strong acids	15.63	84.25	10.27	1.07	2.41	2.00	15.3
6	N	>650° F neutrals	100	-	-	85.33	11.21	0.44	2.59	0.43	5.81
7	N - P/S	>650° F polar/sulfide-free neutrals	100	-	-	86.36	11.15	0.30	1.46	0.73	3.72
8	N + SA1	>650° F neutrals	90.75	>1000° F strong acids	9.25	84.84	10.97	0.51	2.57	1.11	7.64
9	N + SA2	>650° F neutrals	83.31	>1000° F strong acids	16.69	84.45	10.78	0.56	2.55	1.66	9.11
10	N + WA	>650° F neutrals	82.99	>1000° F weak acids	17.01	85.09	10.88	0.64	2.52	0.87	10.6
11	N + DA	>650° F neutrals	85.30	650-1000° F acids	14.70	84.81	10.94	0.69	2.39	1.17	5.66
12	N + SB	>650° F neutrals	86.72	>1000° F strong bases	12.87	84.52	10.92	0.78	2.65	1.13	9.97
13	N + WB	>650° F neutrals	85.31	>1000° F weak bases	14.69	84.43	11.05	0.70	2.70	1.12	8.25
14	N + DB	>650° F neutrals	86.94	650-1000° F bases	13.06	85.13	11.04	0.89	2.41	0.53	5.29

[a] The 2034 gas oil was the only feedstock component not derived from Wilmington crude.

addition to the Wilmington neutrals in order to check for any effects of the diluent (gas oil versus neutrals) on cracking behavior of acid/base fractions.

Table IV shows overall product distributions obtained from each of the feeds in table III. As expected, the yields of gas, gasoline, light cycle oil (LCO), heavy cycle oil (HCO) and coke were quite feedstock dependent. In all cases, the presence of acids or bases increased yields of heavy products (HCO, coke) at the expense of light products (gas, gasoline). Partitioning of nitrogen into liquid product versus coke (formation of gaseous nitrogen products was negligible) was relatively constant, except that feedstocks containing 650-1000° F acids (nos. 2, 4, 5, 11) yielded liquid products somewhat enriched in nitrogen. The presence of acids/bases decreased H_2S formation in the case of 2034 gas oil, which increased relative partitioning of sulfur into liquid products. Since this effect was not observed during cracking of blends of Wilmington neutrals with acid/base fractions, it probably reflects simple carryover of Wilmington acids/bases, which are enriched in sulfur relative to the 2034 gas oil, into the HCO range liquid products from feeds 2 and 3. Sulfur partitioning into liquid products was significantly higher for polar/sulfide-free neutrals compared to whole neutrals. This observation indicates that a higher proportion of sulfide sulfur is converted into H_2S compared to thiophenic forms of sulfur. Sulfur partitioning into coke ranges between 1 and 3 percent for all feeds except the whole Wilmington resid, and the whole resid spiked with strong acids (feeds 4 and 5). Gaseous sulfur (H_2S) partitioning is more difficult to measure experimentally than that for liquid or coke. Thus, the results calculated by difference (far right, table IV) are probably more accurate than the actual GC data shown in the table.

Consideration of the full set of data from the Wilmington cracking series clearly indicated that the bulk of the light products (gas and gasoline) is derived from the neutral components in each feedstock. Acidic and basic components generally produced small amounts of methane and C_2-hydrocarbons and large amounts of coke and heavy liquid components. For example, the gasoline yield equivalent to the concentration of neutrals in each feedstock is nearly constant, as shown in table V. The neutral-equivalent gasoline yield (NEGY) parameter shown in the table was calculated as follows:

$$\mathrm{NEGY} = \frac{G_B}{G_N N_B} \times 100\% \qquad (1$$

G_B = gasoline yield of blend (wt%)

G_N = gasoline yield for pure neutrals (wt%)

N_B = wt fraction of neutrals in blend

Table IV. - Overall Product Distributions (wt%) Obtained from Wilmington Feedstocks at 521 ± 1° C (970° F) and a Cat/oil Ratio of 8.5 ± 0.5[a]

										Nitrogen partitioning[i]		Sulfur partititoning[j]				
Feed[b] Blend No.	Code	Gas[c]	Gasoline[d]	LCO[e]	HCO[f]	Coke	Total	Conv.[g]	G. Eff.[h]	Liquid	Coke	Gas (GC)	Liquid	Coke	Total	Gas (Diff.)[k]
1	2034GO	18.4	42.7	16.7	14.4	8.5	100.6	69.6	61.4	10.6	89.4	68.1	35.6	2.3	106.0	62.1
2	2034 + DA	13.2	39.6	18.9	18.9	7.8	98.4	60.6	65.4	24.1	75.9	58.9	44.3	1.4	104.6	54.3
3	2034 + DB	11.1	33.9	20.4	23.5	9.8	98.7	54.8	61.8	14.5	85.5	48.0	43.5	3.6	95.1	52.9
4	W	11.6	26.7	12.8	21.9	25.7	98.6	64.0	41.7	22.0	78.0	57.6	33.0	7.0	97.6	60.0
5	W + SA	9.3	24.1	13.5	23.2	25.9	96.0	59.3	40.7	28.3	71.7	49.5	33.2	8.9	91.6	57.9
6	N	14.2	41.4	15.7	15.5	13.9	100.7	69.5	59.6	19.9	80.1	69.8	28.8	1.4	100.0	69.8
7	N - P/S	13.0	41.4	16.2	14.9	13.7	99.1	68.1	60.9	21.9	78.1	67.0	37.2	2.5	106.7	60.3
8	N + SA1	15.7	37.4	14.7	12.2	19.9	100.9	73.0	51.3	15.8	84.2	78.0	23.7	2.9	104.6	73.4
9	N + SA2	13.7	35.1	15.5	15.0	19.8	99.1	68.6	51.2	18.8	81.2	67.9	28.3	3.1	99.3	68.6
10	N + WA	14.3	36.1	15.0	14.1	21.5	101.1	71.9	50.1	17.8	82.2	73.0	27.1	3.7	103.8	69.2
11	N + DA	13.6	39.2	15.3	16.2	16.1	100.3	68.8	57.0	30.3	69.7	67.8	29.5	1.0	98.3	69.5
12	N + SB	13.2	33.5	14.4	17.2	20.7	99.0	67.4	49.6	16.6	83.4	64.3	27.8	3.2	95.3	69.0
13	N + WB	12.6	35.6	14.5	16.4	17.6	96.6	65.9	54.1	17.7	82.3	63.7	27.6	3.1	94.4	69.3
14	N + DB	11.5	34.4	16.9	20.8	16.6	100.2	62.4	55.1	24.9	75.1	61.4	32.4	1.4	95.2	66.2

[a] Absolute standard deviations for product yields are ± 1 wt%, total recovered ± 2 wt%, conversion and efficiency ± 2%, N and S partitioning ± 2%.

[b] See table 2 for feed composition.

[c] Includes C_1-C_4 hydrocarbons and H_2S.

[d] ≥ C_5 (82° F)-430° F.

[e] 430-650° F.

[f] >650° F (approx. 650-1000° F).

[g] Conversion = gas + gasoline + coke.

[h] Gasoline efficiency = (gasoline/conversion) x 100%.

[i] Relative proportion of feed nitrogen found in liquid versus coke (formation of NH_3 was negligible). Coke nitrogen calculated by difference.

[j] Relative proportion of feed sulfur found in gas versus liquid versus coke.

[k] Proportion of sulfur in gas calculated by difference. Compare with direct (GC) result.

Table V. - Neutral-equivalent Gasoline Yield (NEGY)[a]

Feed Blend No.	Code	NEGY (%)[b]
1	2034GO	100
2	2034+DA	103
3	2034+DB	89
4	W	99
5	W+SA	105
6	N	100
7	N-P/S	100
8	N+SA1	100
9	N+SA2	102
10	N+WA	105
11	N+DA	111
12	N+SB	93
13	N+WB	101
14	N+DB	96

[a] 2034 GO was assumed to contain 100% neutrals as the basis for calcuation of feeds 1-3. Calculations for feeds 4-14 were based on Wilmington neutral gasoline yields.

[b] Estimated error in NEGY is ±4%.

For the purpose of calculation of NEGY for feedstocks 1-3, the neutral content of the 2034 gas oil was assumed to be 100%. The validity of this assumption is borne out by the low heteroatom content indicated in table III for this material (feedstock 1).

Deviations of NEGY in excess of estimated experimental error (±4%, see footnote in table V) are relatively rare. Low data for selected feedstocks containing basic fractions (feedstocks 3, 12 and 14) may be attributed to the well known ability of basic nitrogen compounds to act as reversible catalyst poisons. Marginally high results for selected feedstocks containing acidic fractions (feedstocks 2, 5, 10, and 11) probably reflect light products formed via cracking of saturated carboxylic acids which are prevalent acidic types in Wilmington crude.[20-23,26]

Thus, a major conclusion from the initial study of Wilmington feedstocks was that light product yields are largely a function of the proportion of neutral components present in the feed. Product distributions from neutral fractions of other resids (plus the whole 2034 gas oil) were similar, as indicated in table VI. The minor variation in gasoline yield from the neutral fractions may be related to hydrogen content or atomic H/(C+S) ratio as shown in figure 3. A more precise relationship could probably be obtained from detailed analysis of the neutral fractions. For comparison, table VII shows product distributions from the corresponding whole resids. Resids containing large proportions of acids and bases (Wilmington and Maya) give corresponding low yields of gasoline, in accordance with the NEGY parameter. The proportion of neutrals present, plus correlations such as those in figure 3, may be used to accurately predict gasoline yield from residual feedstocks. Results from cracking feedstocks in tables VI and VII will be reported in detail in subsequent reports.

Coke yield is approximately linearly related to MCR of feedstocks, as illustrated in figure 4. Data scatter in the figure largely represents specific behavior of acid/base fractions in the feeds, rather than experimental error. When these effects are better understood, a more precise correlation will be derived.

Although product distributions may be adequately modeled from simple feedstock parameters, such as neutral or MCR content, the dependence of product composition on feed composition is more complex. For example, the elemental composition of liquid products from neutrals (table VI) varies significantly, even though yields of liquids are comparable. Table VIII details gasoline composition determined by GC/MS analyses of liquid products from four Wilmington feedstocks. Several conclusions are evident from comparison of gasoline versus feedstock composition, as discussed below.

Table VI. - Overall Product Distributions (wt%) and Elemental Composition of Liquid Products Obtained from Cracking Neutral Fractions[a]

									Whole Liquid Product (wt% Liquids)				
Source	Gas	Gasoline	LCO	HCO	Coke	Total	Conv.	G. Eff.	C	H	N	S	Total
2034GO[b]	18.4	42.7	16.7	14.4	8.5	100.6	69.6	61.4	87.11	12.43	0.022	0.29	99.85
Wilmington	14.2	41.4	15.7	15.5	13.9	100.7	69.5	59.6	87.35	11.65	0.113	1.02	100.13
Maya	16.8	41.0	14.3	11.4	15.2	99.5	73.0	56.2	86.19	12.15	0.016	1.33	99.69
Brass River	17.3	46.3	12.3	18.4	6.9	99.7	68.9	67.2	87.48	13.08	0.0047	0.085	100.65
Lagomedio	16.6	43.4	14.9	14.5	11.8	101.2	71.8	60.5	86.31	12.38	0.012	0.86	99.56

[a] See footnotes in table IV for description of terms and error limits.

[b] Whole gas oil. Other data are for >650° F neutral fractions from the indicated source.

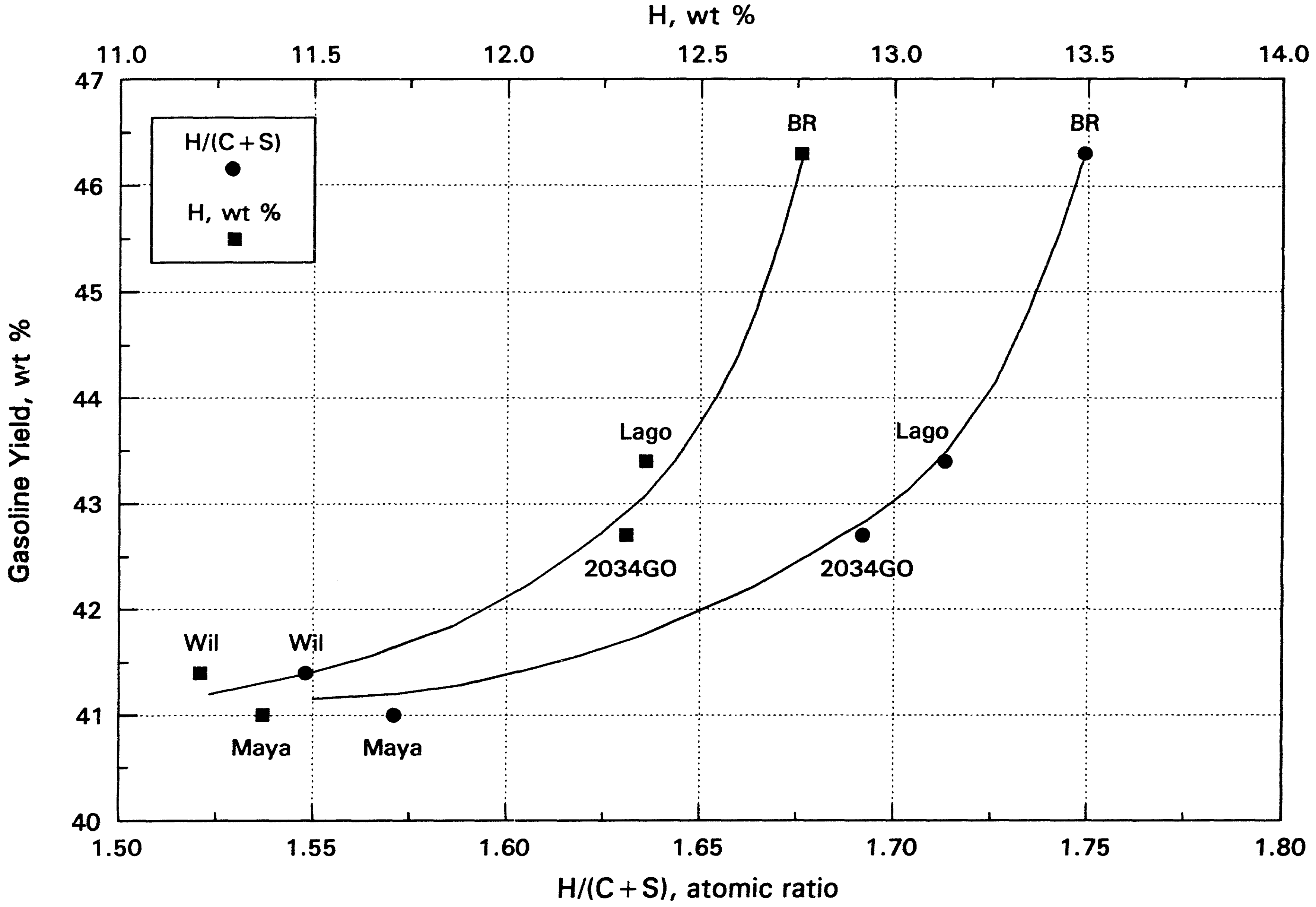


Figure 3. **Gasoline yield obtained at 521° C, cat/oil 8.5 ± 0.5, from neutrals of varying H content (H/(C+S) ratio).**

Table VII. - Overall Product Distributions (wt%) and Elemental Composition of Liquid Products Obtained from Cracking Whole Resids[a]

Resid	Gas	Gasoline	LCO	HCO	Coke	Total	Conv.	G. Eff.	Whole Liquid Product (wt% Liquids)				
									C	H	N	S	Total
2034GO[b]	18.4	42.7	16.7	14.4	8.5	100.6	69.6	61.4	87.11	12.43	0.022	0.29	99.85
Wilmington	11.6	26.7	12.8	21.9	25.7	98.6	64.0	41.7	86.39	11.33	0.376	1.30	99.39
Maya	16.6	28.8	11.8	13.1	30.5	100.9	76.0	37.9	85.79	11.61	0.092	1.72	99.21
Brass River	17.3	47.2	12.1	14.0	8.4	99.1	73.0	64.7	87.30	12.89	0.025	0.076	100.29
Lagomedio	18.5	40.9	12.1	8.1	21.4	100.8	80.7	50.6	86.69	12.26	0.031	0.71	99.69

[a] See footnotes in table IV for description of terms and error limits.

[b] Whole gas oil. Other data are for whole >650° F resids.

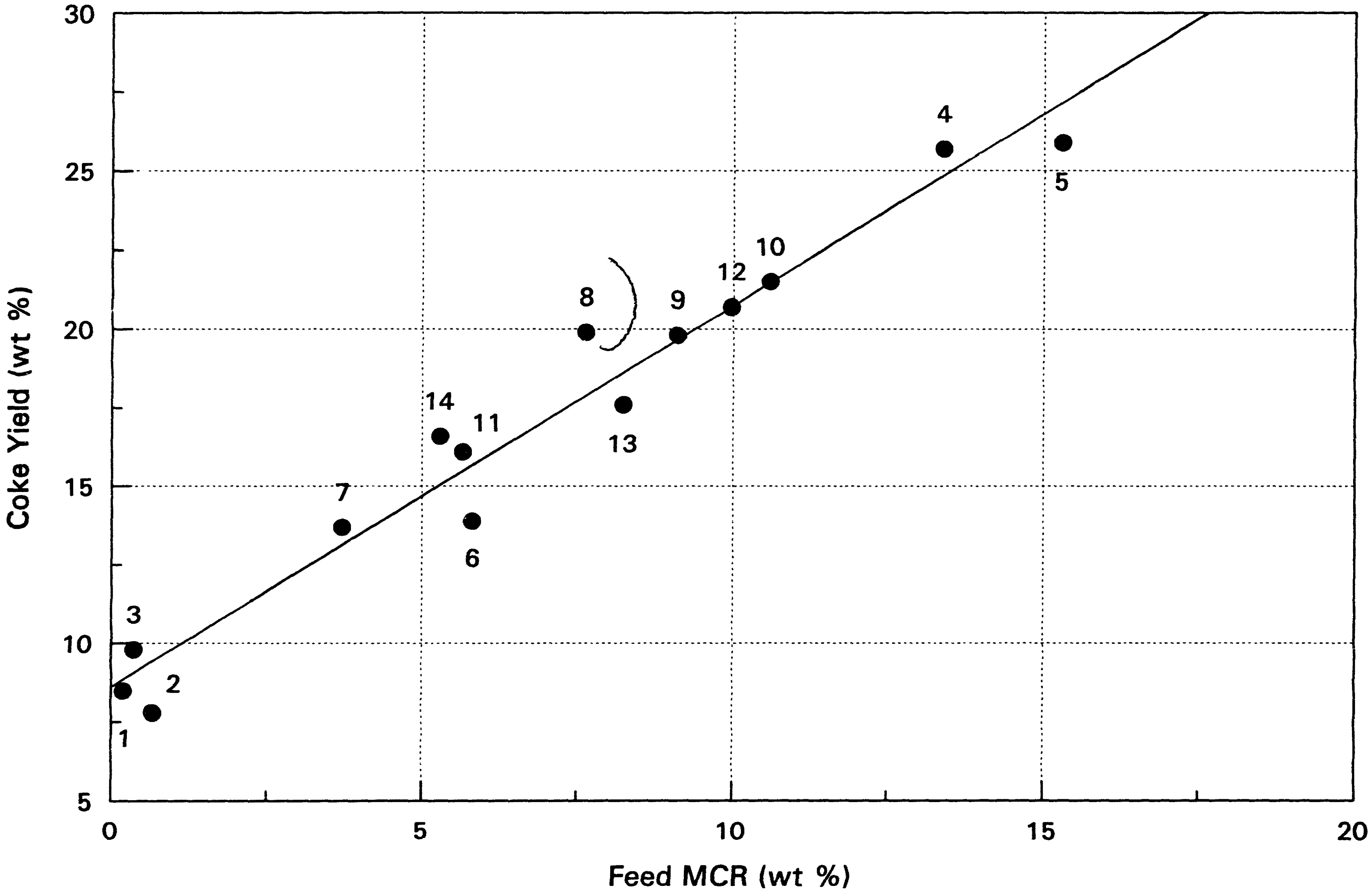


Figure 4. Correlation of coke yield from catalytic cracking versus microcarbon residue (MCR) of feed. Numbers indicate feedstocks listed in Table 4.

Table VIII. - Composition of Gasoline (C_5 - 430° F) from Different Wilmington Feeds (Area%)

FEED	Whole >650° F Resid(4)	>650° F Neutrals (6)	Neutrals + 650-1000° F Acids (11)	Neutrals + 650-1000° F Bases (14)
AROMATICS				
Alkylbenzenes				
benzene	0.14	1.02	1.62	1.78
toluene	5.3	4.3	4.2	4.7
total C_2-benzenes	14.3	11.6	11.2	11.2
ethylbenzene	2.0	1.66	1.65	1.82
o-xylene	3.3	2.9	2.8	2.9
m + *p*-xylenes	9.0	7.0	6.7	6.5
total C_3-benzenes	17.0	14.8	13.7	12.8
isopropylbenzene	0.12	0.028	0.011	0.040
n-propylbenzene	0.99	0.78	0.84	0.87
1-ethyl-2-methylbenzene	1.14	1.02	0.93	0.86
1-ethyl-3-methylbenzene + 1-ethyl-4-methylbenzene	4.3	3.9	3.6	3.2
1,2,3-trimethylbenzene	2.0	1.7	1.6	1.7
1,2,4-trimethylbenzene	5.8	4.9	4.4	4.2
1,3,5-trimethylbenzene	2.6	2.5	2.3	1.9
total C_4-benzenes	9.7	10.8	9.5	7.0
n-butylbenzene	0.51	0.33	0.18	0.13
1-methyl-2-propylbenzene	0.32	0.56	0.51	0.28
1-methyl-3-propylbenzene	0.83	0.79	0.70	0.58
1-methyl-4-propylbenzene	0.18	0.23	0.23	0.47
1,2-diethylbenzene	0.012	0.007	0.014	0.022
1,3-diethylbenzene	0.47	0.67	0.62	0.49
1,4-diethylbenzene	nd[a]	0.06	0.06	0.03
1,2-dimethyl-3-ethylbenzene	0.22	0.48	0.38	0.16
1,2-dimethyl-4-ethylbenzene	1.31	1.52	1.39	1.11
1,3-dimethyl-2-ethylbenzene	0.006	0.09	0.05	0.016
1,3-dimethyl-4-ethylbenzene + 1,4-dimethyl-2-ethylbenzene	1.61	1.82	1.59	1.24
1,3-dimethyl-5-ethylbenzene	1.32	1.38	1.21	0.74
1,2,3,4-tetramethylbenzene	0.63	0.58	0.62	0.25
1,2,3,5-tetramethylbenzene	1.10	1.23	1.07	0.61
1,2,4,5-tetramethylbenzene	0.80	1.01	0.91	0.86
total C_5-benzenes (no. isomers)	3.2 (12)	5.0 (10)	3.4 (12)	2.7 (10)
total C_6-benzenes (no. isomers)	0.30 (1)	0.07 (1)	0.36 (1)	0.17 (3)
Total Alkylbenzenes	49.5	47.6	44.0	40.4

Table VIII. - Composition of Gasoline (C_5 - 430° F) from Different Wilmington Feeds (Area%) (continued)

FEED	Whole >650° F Resid(4)	>650° F Neutrals (6)	Neutrals + 650-1000° F Acids (11)	Neutrals + 650-1000° F Bases (14)
Alkylindans				
indan	0.77	0.92	0.72	0.66
total C_1-indans	3.13	3.12	2.65	2.65
1-methylindan	0.51	0.53	0.47	0.47
4-methylindan	1.51	1.28	1.04	1.39
5-methylindan	1.11	1.31	1.14	0.79
total C_2-indans (no. isomers)	1.41 (4)	1.56 (2)	2.09 (4)	1.66 (4)
Total Alkylindans	5.3	5.6	5.5	5.0
Alkylindenes				
indene	0.14	nd	0.03	0.05
total C_1-indenes	0.02	nd	nd	nd
Total Alkylindenes	0.16	nd	0.03	0.05
Naphthalene	1.26	1.13	0.88	0.58
Alkylthiophenes				
thiophene	0.058	nd	nd	nd
methylthiophene	0.001	nd	nd	nd
Total Alkylthiophenes	0.06	nd	nd	nd
TOTAL AROMATICS	56.3	54.3	50.4	46.0
NORMAL PARAFFINS				
pentane	0.30	0.24	0.36	0.47
hexane	0.56	0.26	0.39	0.50
heptane	1.18	0.26	0.28	0.59
octane	0.94	0.85	0.78	0.96
nonane	0.55	0.32	0.25	0.39
decane	0.58	0.30	0.35	0.58
undecane	0.65	0.47	0.38	0.53
dodecane	0.37	0.056	0.12	0.22
TOTAL N-PARAFFINS	5.1	2.8	2.9	4.2

Table VIII. - Composition of Gasoline (C_5 - 430° F) from Different Wilmington Feeds (Area%) (continued)

FEED	Whole >650° F Resid(4)	>650° F Neutrals (6)	Neutrals + 650-1000° F Acids (11)	Neutrals + 650-1000° F Bases (14)
ISOPARAFFINS				
isopentane	1.03	1.40	1.66	1.14
total C_6	3.0	3.5	4.2	3.3
2,2-dimethylbutane	nd	0.052	0.053	0.092
2,3-dimethylbutane	0.38	0.22	0.42	0.49
2-methylpentane	1.62	1.95	2.16	1.81
3-methylpentane	0.91	1.23	1.54	0.90
total C_7	3.4	3.8	3.8	3.0
2,3-dimethylpentane	0.002	0.013	0.002	0.013
2,4-dimethylpentane	0.040	0.008	0.006	0.008
2-methylhexane	2.02	2.23	2.24	1.77
3-methylhexane	1.33	1.58	1.59	1.23
total C_8	4.3	4.8	4.6	3.5
2,2,3-trimethylpentane	nd	nd	0.004	nd
2,3-dimethylhexane	0.13	0.026	0.021	0.095
2,4-dimethylhexane	0.65	0.80	0.86	0.64
2,5-dimethylhexane	0.32	0.40	0.37	0.35
3,4-dimethylhexane	nd	0.001	nd	nd
2-methylheptane	2.08	1.99	1.92	1.42
3-methylheptane	1.13	1.48	1.46	0.99
4-methylheptane	nd	0.019	nd	0.004
total C_9	2.1	3.2	3.0	1.9
2,3,4-trimethylhexane	nd	nd	0.011	0.013
2,4-dimethylheptane	0.26	0.32	0.34	0.094
2,5-dimethylheptane	0.63	0.89	0.83	0.63
2,6-dimethylheptane	0.36	0.64	0.61	0.45
2-methyloctane	0.19	0.41	0.33	0.13
3-methyloctane	0.70	0.91	0.86	0.64
total C_{10}	0.71	2.4	2.0	1.3
dimethyloctanes (no. isomers)	0.32 (3)	1.77 (5)	1.38 (5)	0.98 (5)
2-methylnonane	0.11	0.14	0.13	0.05
3-methylnonane	0.28	0.43	0.46	0.29
total C_{11} (no. isomers)	0.54 (5)	0.90 (5)	0.88 (6)	0.55 (6)
total C_{12} (no isomers)	0.20 (4)	0.30 (3)	0.32 (4)	0.014 (3)
TOTAL ISOPARAFFINS	15.3	20.3	20.5	14.7

Table VIII. - Composition of Gasoline (C_5 - 430° F) from Different Wilmington Feeds (Area%) (continued)

FEED	Whole >650° F Resid(4)	>650° F Neutrals (6)	Neutrals + 650-1000° F Acids (11)	Neutrals + 650-1000° F Bases (14)
NAPHTHENES				
Saturated				
cyclopentane	0.06	0.87	0.79	1.14
total C_6	1.46	4.9	4.9	5.9
cyclohexane	0.093	3.1	3.0	4.2
methylcyclopentane	1.37	1.76	1.92	1.66
total C_7	2.75	3.3	3.5	2.76
c-1,2-dimethylcyclopentane	0.29	0.40	0.47	0.28
t-1,2-dimethylcyclopentane	0.67	0.58	0.62	0.66
c-1,3-dimethylcyclopentane	0.44	0.61	0.64	0.47
t-1,3-dimethylcyclopentane	0.67	0.79	0.83	0.69
methylcyclohexane	0.68	0.94	0.91	0.66
Total C_5-C_7 Saturated Naphthenes	4.2	9.1	9.2	9.8
One double bond				
cyclopentene	0.21	0.20	0.30	0.49
total C_1-cyclopentenes	2.0	1.03	1.26	2.0
1-methylcyclopentene	1.44	0.51	0.69	1.33
4-methylcyclopentene	0.52	0.52	0.57	0.70
total C_2-cyclopentenes (no. isomers)	2.3 (4)	1.3 (5)	1.8 (4)	4.0 (6)
Total C_0-C_2-Cyclopentenes	4.5	2.5	3.4	6.5
Two double bonds				
cyclopentadiene	0.018	nd	0.008	0.016
total C_6-cyclodienes (no. isomers)	0.20 (3)	0.04 (2)	0.04 (2)	0.075 (2)
total C_7 cyclodienes (no. isomers)	0.02 (1)	nd	nd	0.03 (1)
Total C_5-C_7 Cyclodienes	0.24	0.04	0.05	0.12
TOTAL C_5-C_7 NAPTHENICS[b]	8.9	11.6	12.7	16.4
OLEFINS				
One double bond				
total C_5 olefins	1.65	1.56	2.60	3.3
2-methylbutene-1	0.27	0.23	0.37	0.52
3-methylbutene-1	0.038	0.036	0.057	0.089
2-methylbutene-2	0.74	0.69	1.17	1.34
pentene-1	0.092	0.11	0.18	0.26
c-pentene-2	0.18	0.17	0.26	0.38
t-pentene-2	0.33	0.32	0.56	0.72

Table VIII. - Composition of Gasoline (C_5 - 430° F) from Different Wilmington Feeds (Area%) (continued)

FEED	Whole >650° F Resid(4)	>650° F Neutrals (6)	Neutrals + 650-1000° F Acids (11)	Neutrals + 650-1000° F Bases (14)
total C_6 olefins	2.6	1.8	2.6	3.8
2-methylpentene-1	0.30	0.18	0.13	0.60
3-methylpentene-1	0.029	0.017	0.022	0.022
4-methylpentene-1	0.07	nd	nd	nd
c-3-methylpentene-2	0.50	0.41	0.70	0.84
t-3-methylpentene-2	0.46	0.37	0.46	0.68
c-4-methylpentene-2	nd	nd	0.006	nd
t-4-methylpentene-2	nd	nd	0.006	nd
hexene-1	0.30	0.17	0.09	0.15
c-hexene-2	0.35	0.11	0.39	0.50
t-hexene-2	0.38	0.29	0.55	0.62
c + t-hexene-3	0.19	0.26	0.26	0.41
total C_7 olefins (no. isomers)	1.1 (10)	1.2 (10)	1.6 (5)	1.8 (9)
Total C_5-C_7 Olefins	5.4	4.5	6.8	8.9
<u>Two double bonds</u>				
total C_5 dienes (no. isomers)	0.009(1)	0.003(1)	nd	nd
total C_6 dienes (no. isomers)	0.006(1)	nd	nd	nd
total C_7 dienes (nd isomers)	0.022(1)	0.01 (2)	0.006(2)	0.007 (1)
Total C_5-C_7 Dienes	0.04	0.02	0.006	0.007
TOTAL C_5-C_7 OLEFINICS[b]	5.4	4.5	6.8	8.9
TOTAL ALL CATEGORIES[c]	**91.0**	**93.5**	**93.3**	**90.2**

[a] None detected.

[b] At C_8 and above, naphthenes generally cannot be differentiated from olefins.

[c] Species not accounted for are predominantly $\geq C_8$ naphthenes and olefins.

The distribution of heteroatomic compounds in the feed exerts a greater impact on gasoline product composition than any other single feedstock parameter. For example, the higher concentration of alkylbenzenes and total aromatics from pure neutrals compared to neutral + acid or neutral + base feed reflects the greater activity of the catalyst when the inhibiting acidic or basic compounds are absent. Similarly, the lower concentration of *n*-paraffins left in the pure neutrals product reflects the higher conversion attained with that feed.

Olefins are formed as primary products from all cracking reactions; they undergo subsequent reactions to form isoparaffins, naphthenes and aromatics. As expected, the concentration of olefins is lowest in the gasoline from pure neutrals. The concentration of olefins increases with the other feeds in the following order: whole resid <acid + neutrals <base + neutrals. The relatively low olefin concentration in gasoline from the whole resid stems from a lower primary cracking reaction rate (overall gasoline yield from the whole resid was only 60-70% of that obtained from other feeds) and probable consumption in coke formation (coke yield from the whole resid was 1.5 - 1.8 times that of other feeds). The higher olefin content of base + neutrals compared to acid + neutrals product reflects the greater inhibition of bases on secondary cracking reactions.

The nearly equal concentration of isoparaffins from neutral and acid + neutral feeds indicates minimal acid inhibition of hydrogen transfer to form isoparaffins from the corresponding olefins. The substantially lower isoparaffin content of whole resid and base + neutral products indicates that basic compounds inhibit hydrogen transfer to a much greater extent than acids. Similarly, the ratios of saturated naphthenes to those with one or two double bonds decrease as follows: neutrals (3.6) >acids + neutrals (2.7) >bases + neutrals (1.5) >whole resid (0.9). The very low ratio obtained from the whole resid suggests that formation of high levels of coke on the catalyst further limits hydrogen transfer in addition to inhibition by bases.

The very low benzene, cyclohexane and cyclopentane content of the whole resid gasoline indicates that very little alpha cleavage of alkylbenzenes occurred in that case. This observation is further supported by the relatively high levels of ethyl-, *n*-propyl- and *n*-butylbenzenes observed. The rate of alpha cleavage of aromatics may be sensitive to the amount of coke formed on the catalyst (highest with whole resid) or the presence of higher boiling acid or base compounds (not present in other feeds).

The overall indication is that gasoline range products are largely formed via secondary catalytic reactions from olefins. Polar compounds in the feed control the composition of the resulting gasoline through varying degrees of inhibition of these secondary reactions, as noted above. The hydrocarbon structure of the feed does have some impact on product composition, however. For example, the relatively high alkylbenzene content of the whole resid product must reflect some direct contribution from primary cracking reactions, since the observed degree of inhibition of secondary reactions effectively would prevent attainment of the observed concentration solely through secondary processes (the whole resid is the most aromatic feed, see table III). Other isolated incidences of high concentrations of individual species or isomeric groups (e.g. C_2-indans from acid + neutrals) may reflect a particular aspect of feedstock structure. The relative importance of hydrocarbon structure versus polar compound distributions should become more quantifiable as data on feedstocks from other crudes become available.

Finally, concentrations of unstable hydrocarbon species such as cyclopentadienes and other dienes were lower in gasolines from base-free feeds (neutrals, acid + neutrals). The presence of bases apparently inhibits further reaction of these intermediate species to more stable hydrocarbons. This aspect of composition may be important with respect to gum formation of the gasoline during storage and use since such highly reactive species are usually responsible for fuel quality problems.

The inhibition of cracking by nitrogen bases was investigated further through cracking of blends of 2034 gas oil containing up to 50 wt% of a Wilmington 700-1000° F base fraction. This base fraction was not the same one as used in prior experiments; it was isolated from a different Wilmington crude sample. Its elemental analysis was: 81.90% C, 10.02% H, 2.49% N, 2.57% S and (by difference) 3.02% O. Thus, its nitrogen content was lower and its sulfur and oxygen contents were higher than the prior 650-1000° F base fraction (table II). Use of this alternate base fraction was necessitated by the large quantity of bases (50 g) required for the experiments; the alternate Wilmington fraction was the only one available in that quantity.

Table IX shows the product distributions obtained. The overall conclusion reached was that base inhibition does not continually increase with increasing concentration of basic nitrogen in the feed; rather it attains a limiting value determined by feedstock and catalyst properties. The NEGY data best illustrate this finding; a limiting value of 86 is achieved with feedstocks containing about 30 wt% bases. This result is consistent with the previous NEGY of 89 obtained for feedstock 2 (table 10.4), given the difference in nitrogen contents of the two base fractions employed and the uncertainty (±4) in NEGY data. Since the surface area and hence number of active sites on the catalyst is finite, the above finding is not surprising. However, the consistency with respect to sulfur partitioning was unexpected, since a large proportion of the sulfur in the

Table IX. - Overall Product Distributions (wt%) as a Function of Base Content Obtained at 521 ± 1° C (970° F) and a Cat/oil Ratio of 8.5 ± 0.5[a]

										Nitrogen partitioning[j]		Sulfur partititoning[k]				
Wt% Bases in Feed[b]	Gas[c]	Gasoline[d]	LCO[e]	HCO[f]	Coke	Total	Conv.[g]	G. Eff.[h]	NEGY[i]	Liquid	Coke	Gas (GC)	Liquid	Coke	Total	Gas (Diff.)[l]
0	18.4	42.7	16.7	14.4	8.5	100.6	69.6	61.4	100	10.6	89.4	68.1	35.6	2.3	106.0	62.1
3.00	17.8	40.6	17.5	15.5	9.8	101.2	68.2	59.5	98	11.3	88.7	67.5	32.6	4.0	104.1	63.4
10.00	14.6	38.3	19.0	19.7	9.4	100.2	61.4	62.5	100	16.6	83.4	62.7	35.6	2.6	100.9	61.8
20.00	10.7	32.4	20.9	25.2	11.7	100.9	54.8	59.1	95	23.0	77.0	59.3	38.5	2.1	99.9	59.4
29.91	9.7	25.7	20.0	31.8	13.2	100.4	48.8	52.9	86	31.0	69.0	61.0	36.7	2.4	100.1	60.9
40.00	8.9	22.0	19.2	34.9	14.2	99.2	45.1	48.6	86	42.1	57.9	62.7	34.9	3.5	101.0	61.7
50.00	8.7	19.9	18.5	38.0	14.6	99.7	41.8	46.2	93	49.7	50.3	61.1	38.1	2.2	101.4	59.7

[a] Absolute standard deviations for product yields are ± 1 wt%, total recovered ± 2 wt%, conversion and efficiency ± 2%, NEGY ± 4%, N and S partitioning ± 2%.

[b] Balance of feed is 2034 gas oil..

[c] Includes C_1-C_4 hydrocarbons and H_2S.

[d] $\geq C_5$ (82° F)-430° F.

[e] 430-650° F.

[f] >650° F (approx. 650-1000° F).

[g] Conversion = gas + gasoline + coke.

[h] Gasoline efficiency = (gasoline/conversion) x 100%.

[i] Neutral-equivalent gasoline yield (equation 1).

[j] Relative proportion of feed nitrogen found in liquid versus coke (formation of NH_3 was negligible). Coke nitrogen calculated by difference.

[k] Relative proportion of feed sulfur found in gas versus liquid versus coke.

[l] Proportion of sulfur in gas calculated by difference. Compare with direct (GC) result.

base fraction was of sulfoxide type. Sulfoxide sulfur was originally anticipated to partition differently than the sulfide/thiophenic forms present in the 2034 gas oil.

Figure 5 plots product distribution as a function of base content of feed. The decreasing relative impact of bases on product slate with increasing concentration is evident in the variations in the curves for each product occurring in the 20-30% base content range.

Figure 6 shows the distribution of major gaseous products as a function of base content. The relative decrease in isobutane yield with increasing base content of the feed also levels off in the 20-30% range. Isobutane yield is quite sensitive to catalytic activity. Methane and C_2-gas yields increase with base content; their formation is typically associated with noncatalytic reactions.

Table X lists yields of acid, base and neutral types from LC separations of liquid products completed to date. Yields of neutrals were calculated by difference owing to the large proportion of highly volatile (see table VIII) species present, which were subsequently lost during separation. The acid/base content of all liquid products was significant, even the one obtained from cracking the pure neutral feedstock.

Preliminary GC/MS analysis of trifluoroacetylated acid and base fractions listed in table X showed base fractions to be generally comprised of unconverted, relatively high boiling, species; whereas acid fractions contained a variety of <750° F cracked products. Trace amounts of aniline homologs were the only converted basic species detected. Table XI lists the relative abundance of the major <750° F acidic compound types found in each product. The product containing the highest proportion of a given type is listed as "1"; that with the lowest is assigned "3".

The relatively high proportions of phenol and carbazole homologs present in the product obtained from the feed containing 650-1000° F acids is consistent with the elevated concentrations of likely precursors present in that feedstock. Similarly, the relative abundance of most acidic types is lowest from the netural feedstock. However, the formation of any acidic species from cracking of neutrals may be surprising. The relatively high proportion of indole homologs in the whole resid product is consistent with its higher proportion of diene and other relatively unstable hydrocarbon species in the gasoline fraction (table VIII).

Figure 7 illustrates the GC/MS total ion current (TIC) chromatogram of <750° F components in the acid fraction from the >650° F neutrals feed. The three prominent peaks

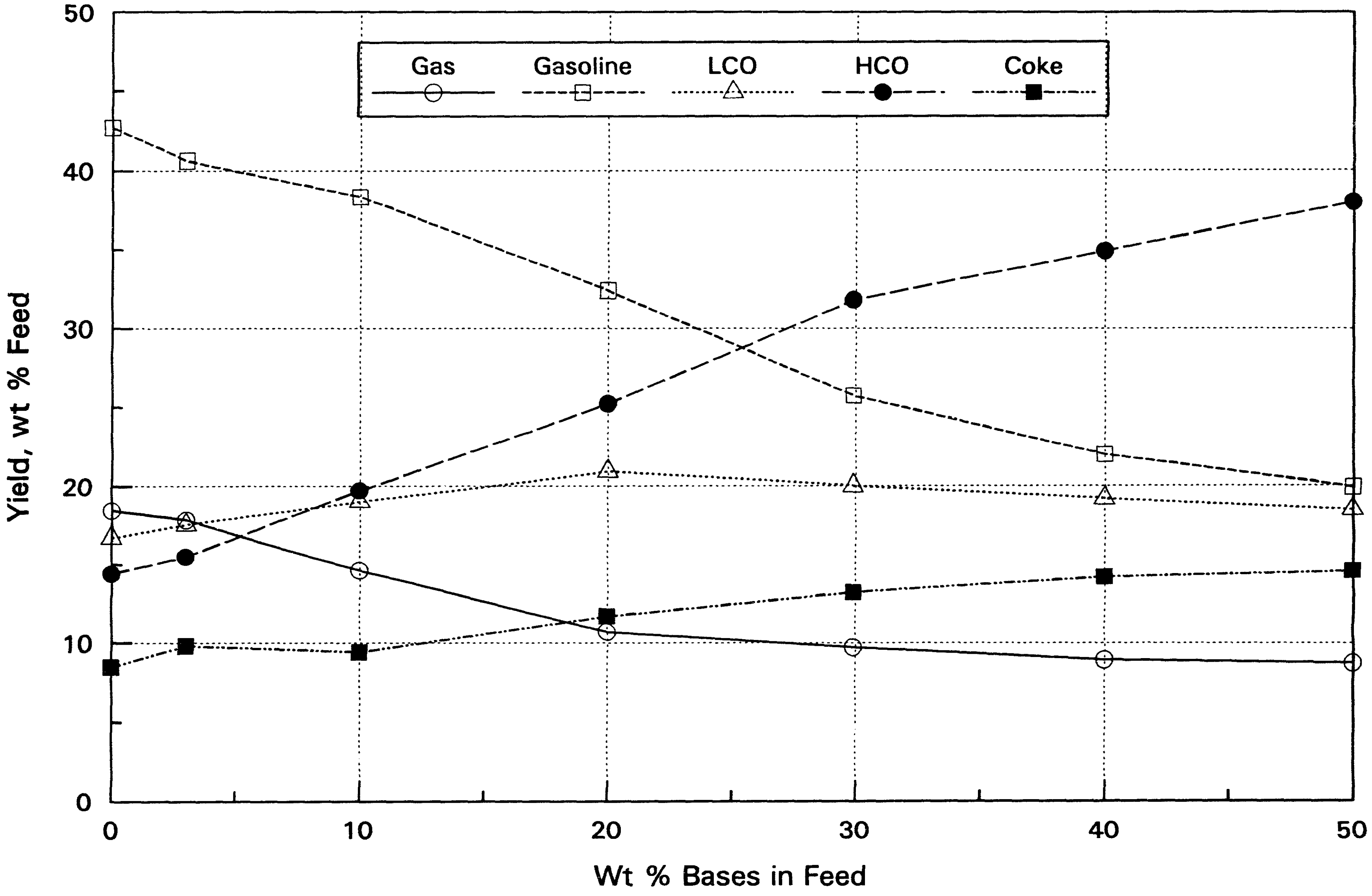


Figure 5. Product distribution as a function of base content (2034GO/Wilmington Base Feedstocks)

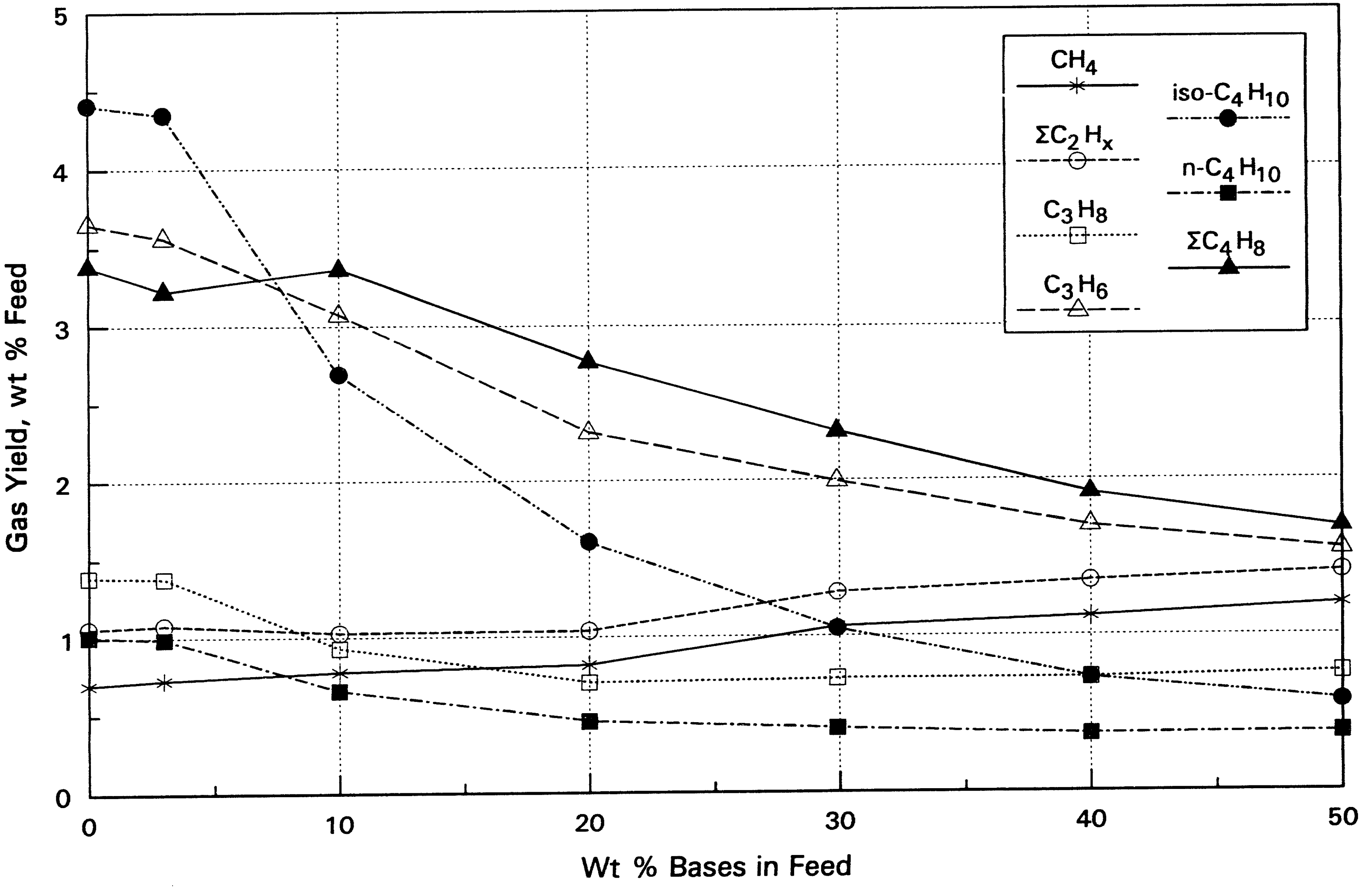


Figure 6. Gas Distribution as a function of base content (2034GO/Wilmington Base Feedstocks)

Table X. - Compound-type Distributions in Liquid Products from Selected Wilmington Feedstocks

	LC Separation Yields (wt%)		
Feed[a]	Acids	Bases	Neutrals[b]
Whole >650° F resid (4)	11.1	4.6	84.3
>650° F Neutrals (6)	5.9	2.1	92.0
Neutrals + 650-1000° F acids (11)	8.7	1.4	89.9

[a] See table III.
[b] By difference.

Table XI. - Relative Abundance of <750° F Compound Types in Acid Fractions Isolated from Selected Whole Liquid Products

	Compound Type			
Feed	Phenols[a]	"$C_8H_{10}S$"[b]	Indoles[c]	Carbazoles[d]
Whole >650° F resid (4)	2	3	1	2
>650° F Neutrals (6)	3	1	3	3
Neutrals + 650-1000° F acids (11)	1	2	2	1[e]

[a] Predominantly phenol and C_1-C_4 alkylphenols.
[b] See figure 7 and accompanying text.
[c] Low levels in all samples; predominantly C_1-C_2-indoles.
[d] Carbazole and C_1-C_4-alkylcarbazoles.
[e] Sample with highest level of 1-substituted carbazoles.

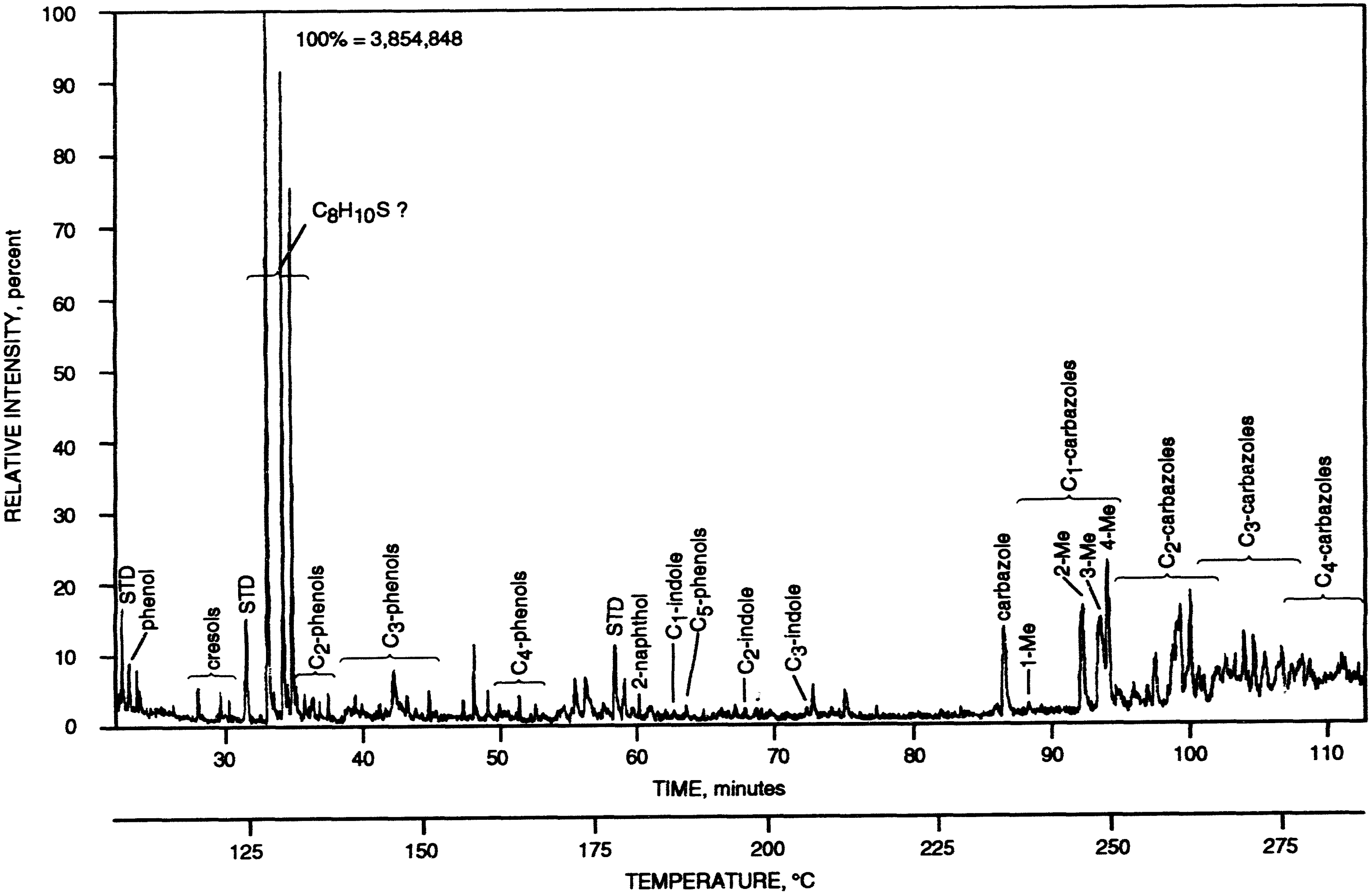
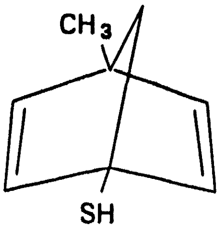


Figure 7. GC/MS total ion current chromatogram of the acid fraction isolated from >650° F Wilmington neutrals liquid product. The alkylcarbazole homologs present are predominantly non-1-substituted isomers. STD = internal standard.

eluting near 130° C may correspond to isomers of an unusual sulfur compund type with a formula of $C_8H_{10}S$. Conventional thiol species exhibiting this formula, such as C_2-thiophenols and methylbenzylmercaptans, have been eliminated as possibilities. In addition, most compounds with formulas of the same nominal molecular weight (138), e.g. $C_8H_{10}O_2$ and $C_9H_{14}O$ types, have similarly been eliminated. The mass spectra of the three components are similar and exhibit the following features: incorporation of one trifluoroacetyl group - thereby indicating one acidic functionality; a fragment corresponding to loss of a methyl group; a base (most intense) fragment occuring at *m/z* 105--129 mass units lower [M–SC(O)CF_3] than the molecular ion (*m/z* 234). A structure consistent with these and other mass spectral features is shown below:



6-mercapto-4-methyl-2,5-norbornadiene

Three isomers, in which both the methyl and mercapto groups are on sp^3 carbons (consistent with the mass spectra), of this basic structure are possible.

The carbazole homologs in the cracked neutrals product may be derived from long chain alkylcarbazoles in the feed which were too sterically hindered and/or too weakly acidic to partition as acids during the initial LC separation of the whole 650-1000° F or >1000° F boiling ranges of Wilmington crude. However, as noted in figure 7, the carbazole homologs detected were predominantly nonhindered (non-1-substituted) species. An effort will be made to identify precursors of important compound types in cracked products, such as carbazole homologs. GC/MS chromatograms of the acid fractions from other liquid products were similar except for the differences in relative proportions of compound types noted in table XI.

DISCUSSION

The available results indicate quite different cracking behavior for neutral compared to acidic or basic components in >650° F resids. The neutral species actively participate in cracking reactions, while acidic/basic components inhibit neutral cracking via competition for active sites on the catalysts and through coke deposition via thermal processes (noncatalytic coke).

Except for the small quantity of distillate hydrocarbon products apparently formed from carboxylic acids - - coke, small quantities of <750° F acids, and gaseous hydrocarbons appear to be the main products from acid/base cracking. This observation is in general agreement with prior studies of the effects of pure nitrogen compounds on gas oil cracking. For example, Fu and Schaffer[11] found that a substantial fraction of a given nitrogen compound spiked into a gas oil feed was recovered in the liquid product. They also found no evidence of dealkylation of nitrogen compounds substituted with short alkylchains. Compounds containing side chains with three or more linear carbons did undergo dealkylation or other reactions involving the alkyl groups.

Given the relatively large hydrocarbon skeleton of acids and bases even in the 650-1000° F boiling range (molecular weight about 350)[19,20] it is somewhat surprising that the influence of the acidic or basic group was sufficiently great to prevent appreciable formation of gasoline or other light products from the bulk hydrocarbon structure of the molecule. Obviously, the focal point of interaction of acids/bases with the catalyst is the functional group; its deactivation of neighboring sites through inductive effects[12] must be sufficient to prevent cracking of other portions of the molecule in contact with those sites. For acids/bases in the >1000° F range, steric exclusion from the interior of the zeolite pores may also have contributed to their lack of conversion to liquid products. Conversion of carboxylic acids probably occurred after thermal decarboxylation; the resulting hydrocarbon reacted in a conventional manner.

Catalyst poisoning from nitrogen compounds has been correlated with gas phase proton affinity.[11] Thus, the greater inhibition by basic compared to acidic nitrogen compounds, and >1000° F strong bases compared to >1000° F weak bases was expected. The greater degree of inhibition with increasing molecular weight (>1000° F compared to 650-1000° F) of basic nitrogen compounds predicted from prior work[11] was not observed here, however. Steric effects or incomplete volatilization of >1000° F base fractions may have decreased their catalyst deactivation capability.

The effects of acid/base compounds on gasoline composition indicated by results in table VIII suggest a greater degree of dependence of product composition on the distribution of polar compounds in feeds than reported previously. Based on those data, the concentration of components with a negative impact on FCC gasoline value (e.g. benzene, dienes, *n*-paraffins) may significantly depend on polar compounds present even in the case of conventional gas oil feeds containing only a few percent acids/bases. Simlarly, storage stability and other utilization parameters of distillate products probably reflect acid/base contents of feedstocks. For example, the concentration of alkylindoles, which are believed to promote sediment formation in diesel fuels,[42,43] clearly depended on feedstock acid/base content (table XI).

The greater relative carryover of sulfur into liquid products from the sulfide/polar-free neutral feed compared to whole neutrals is consistent with prior work indicating a similar trend for hydrotreated feedstocks.[44] Hydrotreating preferentially removes sulfide-type sulfur and therefore gives rise to FCC feeds enriched in thiophenic-type sulfur. The higher relative degree of conversion of sulfide-sulfur to H_2S during cracking is consistent with the lower C-S bond strength of sulfides compared to thiophenes. The lower conversion of sulfoxide-sulfur prevalent in base fractions (table IV) relative to neutral sulfide-sulfur probably relates to the general inertness of polar compounds to cracking, as discussed above. The potential formation of small quantities of mercaptans noted in table XI and figure 7 may reflect reaction of H_2S with hydrocarbon radicals and/or other cracking intermediates.

The approximately linear dependence of coke yield on MCR of feedstocks (figure 4) effectively kills feasibility of selective removal of compound types in resids to improve cracking performance. The MCR of all >1000° F acid/base fractions (table II) is sufficiently great that their removal must be substantially complete before Wilmington >650° F resid could be considered a viable FCC feedstock. Thus, the major value of this work will probably be in elucidation of the effects of polar compounds on FCC product slate and liquid composition which could be used in optimization of conditions for cracking conventional feedstocks or upgraded heavy oil feedstocks.

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REFERENCES

1. Rush, J. B. *Chem. Eng. Prog.* **1981**, *77* (12), 29-32.
2. Avidan, A. A.; Edwards, M.; Owen, H. *Oil Gas J.* **1990**, *Jan. 8*, 33-58.
3. Nieskens, M. J. P. C.; Khouw, F. H. H.; Borley, M. J. H.; Roebschlaeger, K.-H. W. *Oil Gas J.* **1990**, *June 11*, 37-44.
4. Letzsch, W.; Mauleon, J.-L.; Long, S. *Prepr.–Am. Chem. Soc., Div. Pet. Chem.* **1983**, *28*, 944-952.
5. Weekman, V. W., Jr. *AIChE Monogr. Ser.* **1979**, *75* (11), 29 pp.
6. Corma, A.; Wojciechowski, B. W. *Catal. Rev. Sci. Eng.* **1985**, *27* (1), 29-150.
7. Venuto, P. B.; Habib, E. T. *Catal. Rev. Sci, Eng.* **1978**, *18 (1)*, 1-150.
8. Jacob, S. M.; Gross, B.; Voltz, S. E.; Weekman, V. W., Jr. *AIChE J.*, **1976**, *22*, 701-713.
9. Ng, S. H.; Rahimi, P. M. *Energy Fuels* **1991**, *5*, 595-601.
10. Wenig, R. W.; White, M. G.; McKay, D. L. *Prepr.–Am. Chem. Soc., Div. Pet. Chem.* **1983**, *28*, 909-919.
11. Fu, C.-M.; Schaffer, A. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 68-75.
12. Corma, A.; Fornes, V.; Monton, J. B.; Orchilles, A. V. *Ind. Eng. Chem. Res.* **1987**, *26*, 882-886.
13. Scherzer, J.; McArthur, D. P. *Oil Gas J.* **1986**, *Oct. 27*, 76-82.
14. Scherzer, J.; McArthur, D. P. *Ind. Eng. Chem. Res.* **1988**, *27*, 1571-1576.
15. Snyder, L. R. *Anal. Chem.* **1969**, *41*, 314-323.
16. Snyder, L. R.; Buell, B. E.; Howard, H. E. *Anal. Chem.* **1968**, *40*, 1303-1317.
17. Snyder, L. R. *Anal. Chem.* **1969**, *41*, 1084-1094.
18. Snyder, L. R. *Acc. Chem. Res.* **1970**, *3*, 290-299.
19. McKay, J. F.; Weber, J. H.; Latham, D. R. *Anal. Chem.* **1976**, *48*, 891-898.
20. McKay, J. F.; Cogswell, T. E.; Weber, J. H.; Latham, D. R. *Fuel* **1975**, *54*, 50-61.
21. McKay, J. F.; Amend, P. J.; Harnsberger, P. M.; Cogswell, T. E.; Latham, D. R. *Fuel* **1981**, *60*, 14-16.
22. McKay, J. F.; Harnsberger, P. M.; Erickson, R. B.; Cogswell, T. E.; Latham, D. R. *Fuel* **1981**, *60*, 17-26.
23. McKay, J. F.; Latham, D. R.; Haines, W. E. *Fuel* **1981**, *60*, 27-32.
24. Dooley, J. E.; Hirsch, D. E.; Thompson, C. J. *Hydroc. Process.* **1974**, *63* (7), 141-146.
25. Green, J. B.; Hoff, R. J.; Woodward, P. W.; Stevens, L. L. *Fuel* **1984**, *63*, 1290-1301.
26. Bhan, O. K.; Green, J. B.; Brinkman, D. W. *Prepr.–Am. Chem. Soc., Div. Pet. Chem.* **1987**, *32*, 361-368.

27. Sturm, G. P., Jr.; Green, J. B.; Tang, S. Y.; Reynolds, J. W.; Yu, S. K.-T. *Prepr.–Am. Chem. Soc., Div. Pet. Chem.* **1987**, *32*, 369-378.
28. Pearson, C. D.; Green, J. B. *Fuel* **1989**, *68*, 465-474.
29. Green, J. B.; Yu, S. K.-T.; Pearson, C. D.; Reynolds, J. W. *Energy Fuels* **1993**, *67*, 119-126.
30. Green, J. B.; Shay, J. Y.; Reynolds, J. W.; Green, J. A.; Young, L. L.; White, M. E. *Energy Fuels* **1992**, *6*, 836-844.
31. Wells, J. W. *Prepr.–Am. Chem. Soc., Div. Petrol. Chem.* **1987**, *32*, 699-702.
32. Green, J. A.; Green, J. B.; Grigsby, R. D.; Pearson, C. D.; Reynolds, J. W.; Shay, J. Y.; Sturm, G. P., Jr.; Thomson, J. S.; Vogh, J. W.; Vrana, R. P.; Yu, S. K.-T.; Diehl, B. H.; Grizzle, P. L.; Hirsch, D. E. Hornung, K. W.; Tang, S.-Y.; Carbognani, L.; Hazos, M.; Sanchez, V. *Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum*; Topical Report NIPER-452, NTIS No. DE900000200; NTIS: Springfield, VA, 1989; Chapters 1 and 2.
33. Green, J. A.; Green, J. B.; Grigsby, R. D.; Pearson, C. D.; Reynolds, J. W.; Shay, J. Y.; Sturm, G. P., Jr.; Thomson, J. S.; Vogh, J. W.; Vrana, R. P.; Yu, S. K.-T.; Diehl, B. H.; Grizzle, P. L.; Hirsch, D. E. Hornung, K. W.; Tang, S.-Y.; Carbognani, L.; Hazos, M.; Sanchez, V. *Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum*; Topical Report NIPER-452, NTIS No. DE900000201; NTIS: Springfield, VA, 1989; Chapter 5B.
34. McKay, D. L.; Bertus, B. J. *Prepr.–Am. Chem. Soc., Div. Petrol. Chem.* **1979**, *24*, 645-652.
35. Lee, F.-M. *Ind. Eng. Chem. Res.* **1989**, *28*, 542-546.
36. Lee, F.-M. *Ind. Eng. Chem. Res.* **1989**, *28*, 920-925.
37. Wells, J. W.; Zagula, E. J. *Catalytic Cracking of a Wilmington Vacuum Gas Oil and Selected Hydrotreated Products*; Topical Report NIPER-210, 1985.
38. Wells, J. W.; Zagula, E. J.; Brinkman, D. W.; Anderson, R. P. *Catalytic Cracking of Mayan Gas Oil and Selected Hydrotreated Products*; Topical Report NIPER-280, 1987.
39. Green, J. B.; Yu, S. K.-T; Vrana, R. P. GC/MS Analysis of Phenolic Compounds in Fuels after Conversion to Trifluoroacetate Esters. *Submitted to J. High Resolut. Chromatogr.*, **1993**.
40. Green, J. B.; Yu, S. K.-T, Vrana, R. P. GC/MS Analysis of Carboxylic Acids in Petroleum after Esterification with Fluoroalcohols. *Submitted to J. High Resolut. Chromatogr.*, **1993**.
41. Thomson, J. S., Green, J. B.; McWilliams, T. B.; Yu, S. K.-T. Analysis of Amines in Petroleum. *Submitted to J. High Resolut. Chromatogr.*, **1993**.

42. Pedley, J. F.; Hiley, R. W.; Hancock R. A. *Fuel* **1988**, *67*, 1124-1130.
43. Pedley, J. F.; Hiley, R. W.; Hancock R. A. *Fuel* **1989**, *68,* 27-31.
44. Campagna, R. J.; Krishna, A. S.; Yanik, S. J. *Prepr.–Am. Chem. Soc., Div. Pet. Chem.* **1983**, *28*, 894-907.

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