Results and Discussion

ANALYSES

The laboratory analyses were selected to cover the ASTM D 975 specification properties and to measure gross chemical composition categories, which correlate most strongly with performance and emissions. The set of ASTM tests in Figure 1 were applied to the cuts from fractional distillation. Table 7 presents a partial list of the results, with the complete set in Appendix A.

Aromatics

Figure 6 shows the effect of hydrotreating the LCGO as reflected in the changing aromatic carbon distribution. The curve for the feedstock shows high aromatics across the boiling range with increasing values in the high end of the curve. This result is one reason that some people have suggested a limitation of the 90% distillation temperature as a way of reducing particulate emissions. Mild hydrotreating to reduce sulfur concentration lowered the curve about 20%. High severity hydrotreating made the desired reduction in aromatics, but made the greatest reductions in the upper end of the boiling range representing polycyclic aromatics, which contribute most strongly to particulate emissions. The distribution of aromatics by all of the fuels are presented in Figures 7 to 9. Figure 10 details the distribution of aromatic carbon by UV for LCO by ring type and processing severity
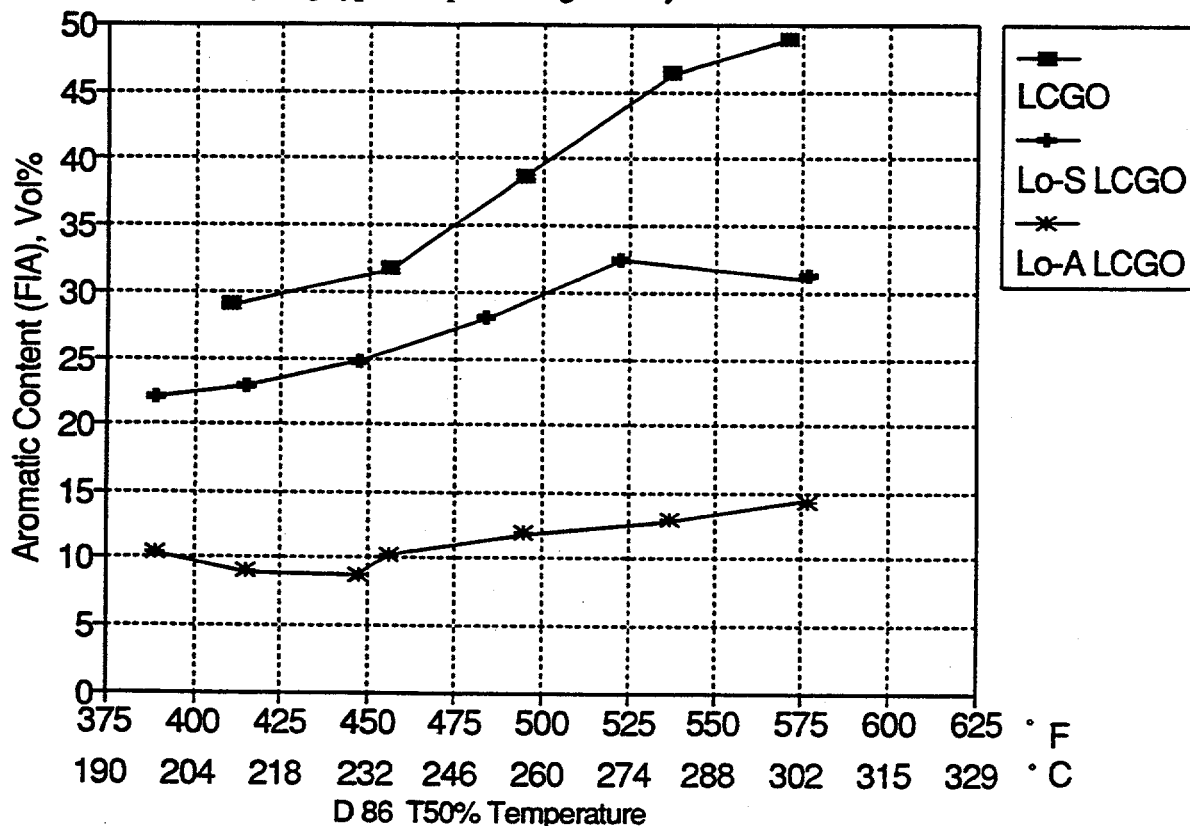

Figure 6. Aromatic carbon versus the 50% point temperature for LCGOs

The trend for high-severity hydrogenation to limit total aromatics showed the greatest decrease in polycyclics. The overall reduction in monocyclic aromatics was slightly greater for higher boiling ranges.

16

Table 7. Partial Results for Distillation Fractions

Property	Feed	#1	#2	#3	#4	#5	#6	#7	#8
STRAIGHT-RUN DIESEL									
Specific Gravity	0.8458	0.8146	0.8445	0.8483	0.848	0.845	0.847	0.859	0.863
Distribution °F	241/288	170/207	241/249	252/259	268/273	284/288	303/307	325/328	352/356
T10/T50 °C	116/142	426/97	116/121	122/126	131/134	140/142	150/152	163/164	178/180
T90/EP °F	335/356	233/246	261/268	269/276	283/291	296/302	314/321	334/339	364/370
°C	168/180	112/119	127/131	132/136	139/144	147/150	157/161	168/171	184/188
Cetane Index D976/D4737	52.6/54.6	41.4/41.5	44.8/45.1	46.0/47.0	49.0/52.2	52.8/59.3	54.5/64.8	52.7/66.2	52.0/80.7
LOW-AROMATIC STRAIGHT-RUN DIESEL									
Specific Gravity	0.8280	0.7892	0.8251	0.8373	0.8368	0.8304	0.8203	0.8314	0.8373
Distribution °F	228/282	116/137	197/207	227/233	250/257	277/281	297/303	324/327	356/362
T10/50 °C	109/139	47/58	92/97	108/112	121/125	136/138	147/151	162/164	180/183
T90/EP °F	328/351	162/177	226/235	246/253	266/274	289/294	308/314	333/338	371/379
°C	164/177	72/81	108/113	119/123	130/134	143/146	153/157	167/170	188/193
Cetane Index D976/D4737	57.7/60.1	13.0/23.8	37.4/38.1	42.6/42.7	49.3/51.3	56.7/64.1	62.1/78.4	61.7/81.5	60.5/82.2
LIGHT-CYCLE OIL									
Specific Gravity	0.9490	0.8849	0.9147	0.9321	0.9440	0.9541	0.9685	0.9979	NS
Distribution °F	247/280	196/210	231/237	251/254	268/272	287/289	306/309	339/344	NS
T10/T50 °C	119/138	91/99	111/114	122/123	131/133	142/143	152/154	171/173	
T90/EP °F	334/365	228/256	245/256	259/270	277/284	294/302	313/323	358/390	NS
°C	168/185	109/124	118/124	126/132	136/140	146/150	156/162	181/199	
Cetane Index D976/D4737	26.1/23.8	20.2/19.4	22.6/17.8	23.8/17.5	25.5/18.6	26.7/20.1	26.9/20.2	24.9/20.6	NS
LOW-SULFUR LIGHT-CYCLE OIL									
Specific Gravity	0.9200	0.8849	0.9082	0.9153	0.9230	0.9352	0.9484	0.9497	NS
Distribution °F	239/270	188/218	229/242	244/253	262/271	284/292	313/317	343/351	NS
T10/T50 °C	115/132	87/103	109/117	118/123	128/133	140/144	156/158	173/177	NS
T90/EP °F	323/361	243/266	261/284	272/287	287/300	394/313	325/332	372/392	NS
°C	162/183	117/130	127/140	133/142	142/149	201/156	163/167	189/200	NS
Cetane Index D976/D4737	43.5/44.1	36.4/37.4	38.0/38.2	40.7/40.5	42.7/42/7	44.5/45.5	47.2/52.6	NS	NS

NS - No Sample

Table 7. Partial Results for Distillation Fractions
(Continued)

Property	Feed	#1	#2	#3	#4	#5	#6	#7	#8
LOW-AROMATIC LIGHT CYCLE OIL									
Specific Gravity	0.8628	0.8479	0.8623	0.8676	0.8708	0.8745	0.8703	0.8448	NS
Distribution °F	215/253	183/196	211/217	230/234	247/252	268/271	286/282	319/327	NS
T10/50 °C	102/123	84/91	99/103	110/112	119/122	131/133	141/139	159/164	NS
T90/EP °F	305/347	208/215	222/234	243/254	259/268	277/284	294/301	354/379	NS
°C	152/175	98/102	106/112	117/123	126/131	136/140	146/149	179/193	NS
Cetane Index D976/D4737	40.1/39.8	24.6/24.5	28.8/26.5	33.3/31.0	37.4/35.3	40.9/40.3	45.0/47.3	56.9/72.3	NS
LIGHT-COKER GAS OIL									
Specific Gravity	0.8676	0.8403	0.8565	0.8740	0.8871	0.8927	0.9094	NS	NS
Distribution °F	224/256	202/210	230/236	252/256	277/281	296/299	317/321	NS	NS
T10/T50 °C	107/124	94/99	110/113	122/124	136/138	147/148	158/161	NS	NS
T90/EP °F	301/320	221/238	245/255	264/274	286/296	304/313	329/341	NS	NS
°C	149/160	105/114	118/123	129/134	141/147	151/156	165/172	NS	NS
Cetane Index D976/D4737	39.3/38.9	33.3/32.6	37.0/35.6	37.9/36.0	39.2/38.3	40.6/41.8	38.8/41.6	NS	NS
LOW-SULFUR LIGHT-CYCLE GAS OIL									
Specific Gravity	0.8463	0.8184	0.8299	0.8403	0.8524	0.8628	0.8697	NS	NS
Distribution °F	219/247	182/198	204/213	222/231	245/251	267/273	297/303	NS	NS
T10/T50 °C	104/119	83/92	96/101	106/111	118/122	131/133	147/151	NS	NS
T90/EP °F	289/315	219/236	228/242	245/256	262/274	282/288	314/329	NS	NS
°C	143/157	104/113	109/117	118/124	128/134	139/142	157/165	NS	NS
Cetane Index D976/D4737	43.5/44.1	36.4/37.4	38.0/38.2	40.7/40.5	42.7/42.7	44.5/45.5	47.2/52.6	NS	NS

NS - No Sample

Table 7. Partial Results for Distillation Fractions
(Continued)

| Property	Feed	#1	#2	#3	#4	#5	#6	#7	#8
LOW-AROMATIC LIGHT-CYCLE OIL									
Specific Gravity	0.8393	0.8203	0.8265	0.8324	0.8418	0.8490	0.8498	0.8524	NS
Distribution °F	224/255	190/199	207/214	225/231	246/251	264/269	287/291	315/317	NS
T10/T50 °C	107/124	88/93	97/101	107/111	119/122	129/132	142/144	157/158	NS
T90/EP °F	302/322	212/221	227/241	242/252	262/271	277/286	297/301	328/340	NS
°C	159/161	100/105	108/116	117/122	128/133	136/141	147/149	164/171	NS
Cetane Index D976/D4737	48.0/49.2	36.1/36.6	39.7/39.9	43.6/44.0	46.1/47.2	47.9/50.3	51.7/57.7	53.8/65.9	NS
FISCHER-TROPSCH 1									
Specific Gravity	0.7770	0.7538	0.7633	0.7710	0.7783	0.7853	0.7913	0.7989	NS
Distribution °F	208/261	179/189	203/213	226/234	248/254	272/277	292/297	319/324	NS
T10/T50 °C	98/127	82/87	95/101	108/112	120/123	133/136	144/147	159/162	NS
T90/EP °F	311/327	216/236	233/246	246/253	264/272	285/292	304/309	331/337	NS
°C	155/164	102/113	112/119	119/123	129/133	141/144	151/154	166/169	NS
Cetane Index D976/D4737	75.4/81.4	62.7/67.2	67.9/73.3	71.0/78.9	73.2/84.2	74.9/90.4	75.1/95.4	74.6/102.2	NS
FISCHER-TROPSCH 2									
Specific Gravity	0.8081	0.7783	0.7936	0.8058	0.8086	0.8104	0.8132	0.8146	NS
Distribution °F	406/509	274/306	334/354	380/403	424/442	468/489	514/537	557/571	NS
T10/T50 °C	208/265	134/152	168/179	193/206	218/228	252/254	268/281	292/299	NS
T90/EP °F	588/627	354/392	395/428	442/537	470/522	508/526	553/565	585/603	NS
°C	309/331	179/200	202/220	228/281	243/272	264/274	289/296	307/317	NS
Cetane Index D976/D4737	62.2/64.6	28.9/35.3	37.3/40.5	44.7/46.2	51.6/53.8	58.6/63.2	63.2/72.3	65.5/80.1	NS

NS - No Sample
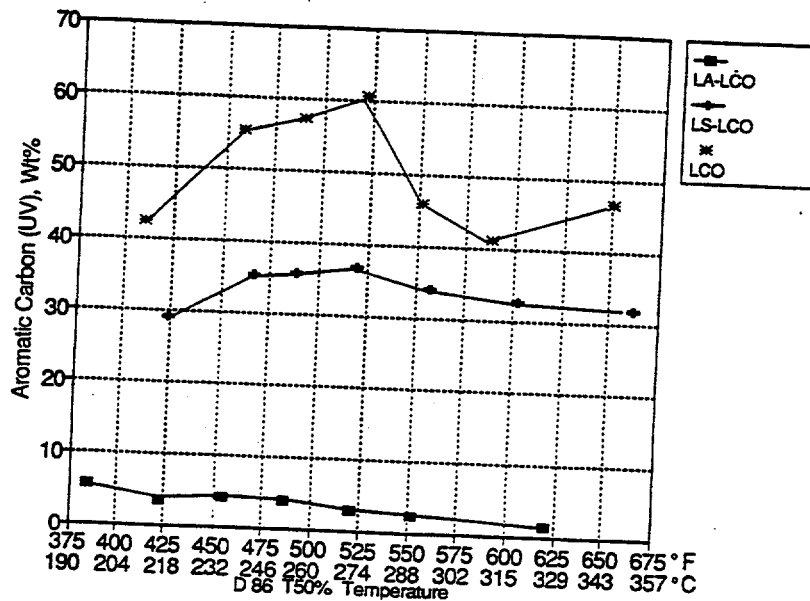
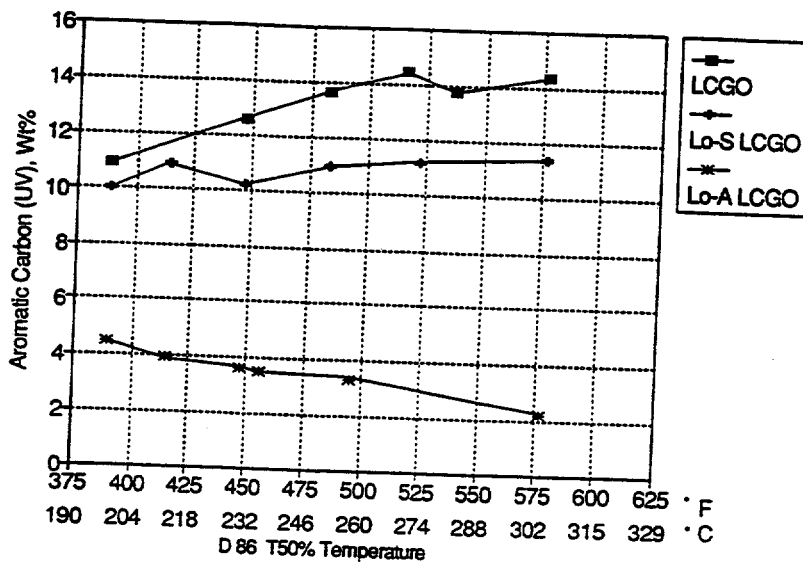**Figure 7. Aromatics vs boiling point for the LCOs**

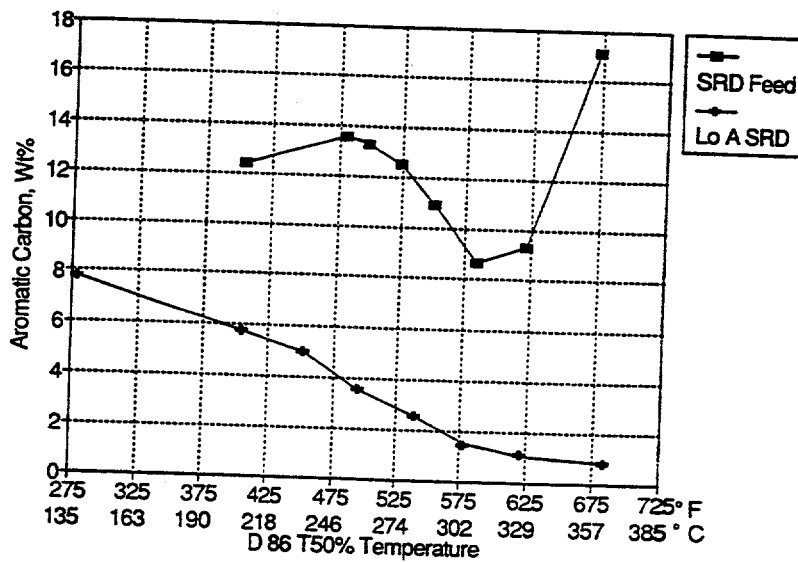**Figure 8. Aromatics vs boiling point for the LCGOs**

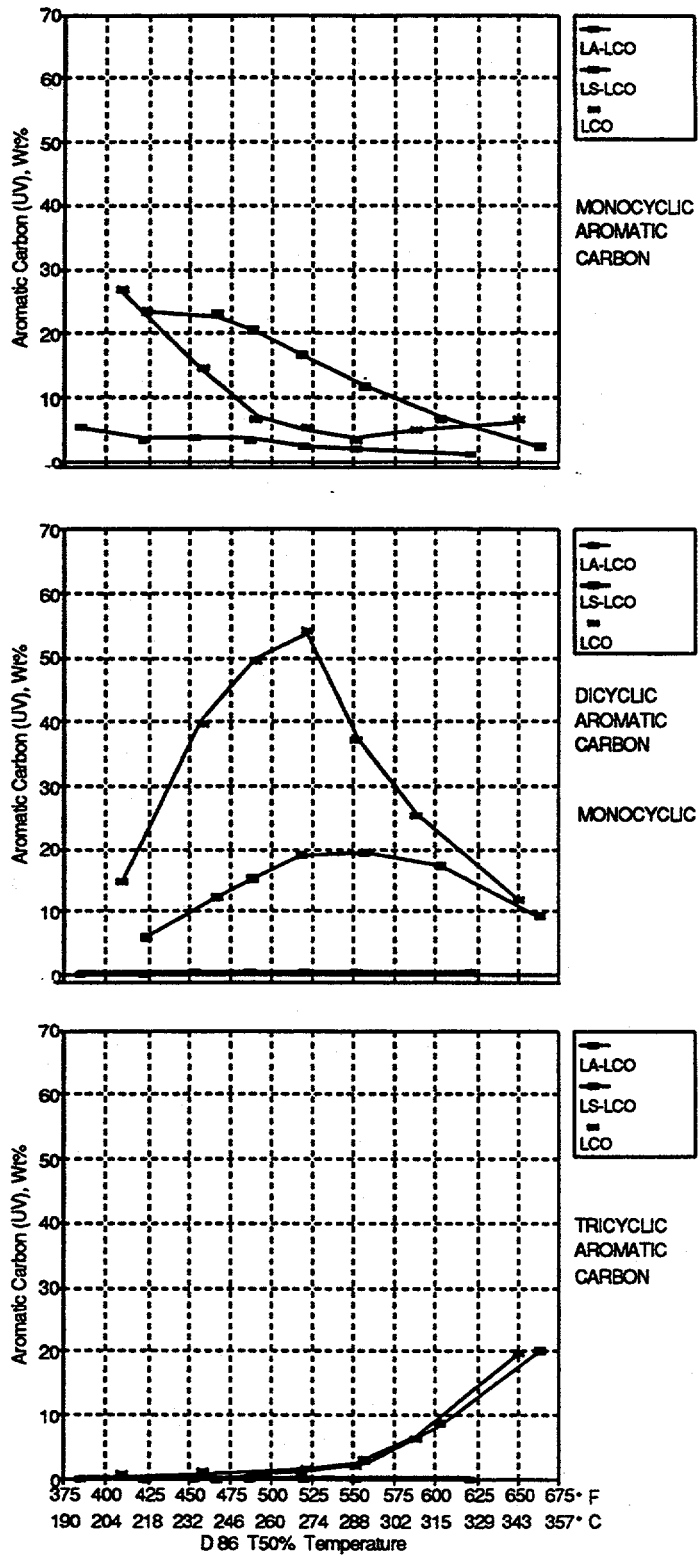**Figure 9. Aromatics vs boiling point for the SRDs**

20

Figure 10. LCO aromatics distribution

21

The aromatics are uniformly distributed over the boiling range for the light-cycle oils, as seen in Figure 7. Moderate hydrotreatment accomplished significant reduction of the sulfur without a significant effect on the aromatics content. Severe hydrotreating had a significant effect on the aromatics, and hydrotreating was effective in reducing the aromatics over the entire boiling range, as seen in Figure 7.

The results for the light-coker gas oils presented in Figure 8 indicate that the aromatics are concentrated in the heavier fractions, at least for the raw material. Hydrotreating first to the low-sulfur level and then for reduced aromatics was effective in lowering the aromatic content of the heavier fractions.

The aromatic content of the straight-run diesel fuel is uniformly distributed across the boiling range. Unlike the higher aromatic content light-cycle oil, however, hydrotreating was much more effective in reducing the aromatics content of the heavier fractions.

The results for aromatic composition of the LCO are presented in the series of graphs of Figure 10. This series of graphs is representative of the changes made by hydrogenation. The total aromatic carbon was reduced moderately in concentration as the sulfur was reduced by low severity treatment. The distribution of aromatics decreased most in the highest-boiling point fractions, which display the most tricyclic compounds. A similar decrease is noted for dicyclic aromatics, but monocyclics increase across the boiling range. In addition to creating corresponding cycloparaffins from the two- and three-ring aromatics, the hydrogenation opened rings in the multicycles to form alkylbenzenes distributed throughout the lower boiling ranges.

The above results suggest that hydrotreating could be used more effectively to reduce the aromatics content of fuels if selected fractions of certain feedstocks are treated. The results also suggest that the proposed reductions in the end point of diesel fuels for emission control will have a significant effect on the aromatics content of fuels from selected feedstocks, in addition to the benefits obtained from the decrease in volatility.

Cetane Index

The plot of cetane index versus 50% recovered temperatures (T50) by D 86 in Figure 11 was made by two estimating methods — ASTM D 976 and D 4737. Both correlations use density and T50, but in different ways. D 976 uses API gravity and T50 in two terms, while D 4737 uses specific gravity and T50 in four terms. Furthermore, the new four-term correlation used a larger fuel matrix including cracked components and shale oil to develop its correlation. D 4737 gave lower cetane index in the front end of the boiling range and higher estimates in the back end. These calculations may be compared with the CVCA and VCR results below where the fractions at highest boiling ranges increased the most in ignition quality from the whole fuel. This is consistent with the results of Weidmann et al., (1988) for full-boiling test fuels.
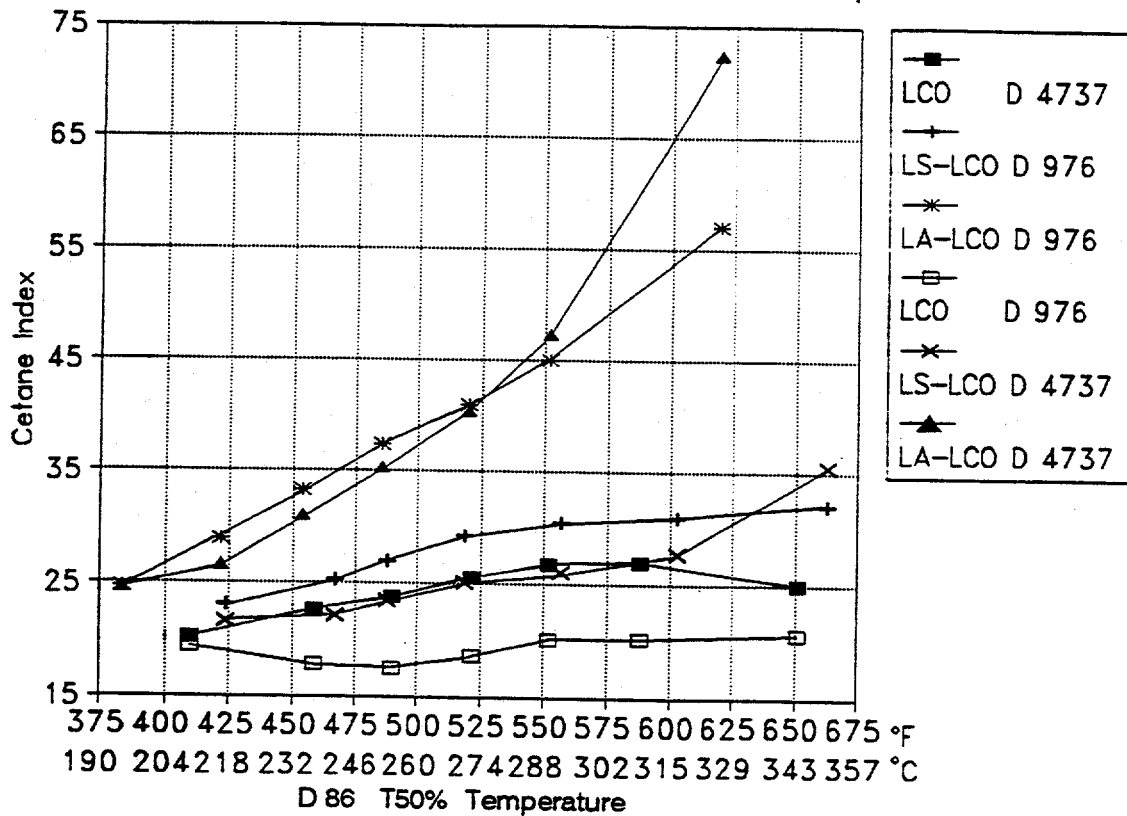
Figure 11. Cetane index by ASTM D 976 and D 4737 versus LCO D 86 50% temperature

The corresponding results for cetane index of the LCGO and its hydrotreated products are presented in Figure 12.
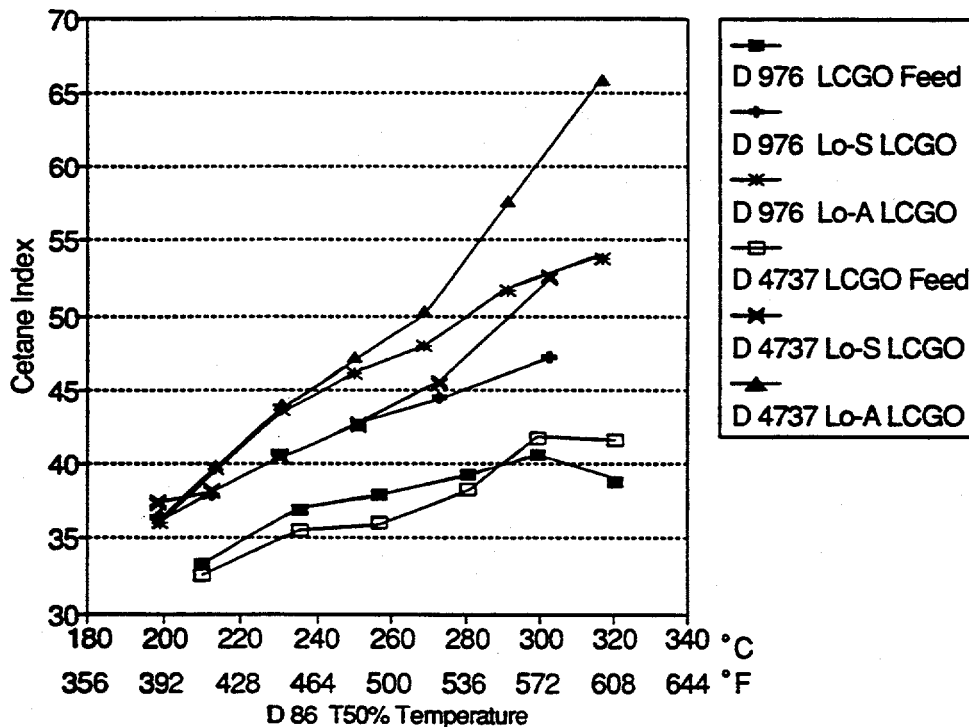

Figure 12. Cetane index versus the 50-percent point for the LCGOs

23

CVCA RESULTS

The early goals of the CVCA development work included both the short-term goal of determining cetane number and the broader goal of providing an improved measure of ignition-quality specification. The CVCA was also developed to rate nonspecification fuel. For the latter goal, we measured the ignition delay times on each test material at three initial temperatures (427°, 482°, and 582°C) and constant density.

The data generated at these initial temperatures were used to examine the Arrhenius nature of the ignition data. In addition, we used these data to examine a potential technique for directly rating the cold-start characteristics of fuels for diesel engines. In this cold-start study, calibrations using several different blends of the primary reference fuels were generated at each of the three different initial temperatures. The lower temperatures were selected to correspond to compression temperature during cold start, and the higher temperatures were selected to correspond to the estimated range of compression temperatures in the standard CFR engine during a fuel cetane rating evaluation.

The test fuels were rated using the three test conditions and calibrations. The effects of the three different initial temperatures are demonstrated in Figure 13 for the same blends of the primary reference fuels. The data have been reduced to hyperbolic form in terms of cetane number as functions of the ignition delay times. The results of this comparison indicate that even the *primary reference fuels* for cetane rating display different relationships between the cetane number and the ignition delay, depending upon the test temperature.
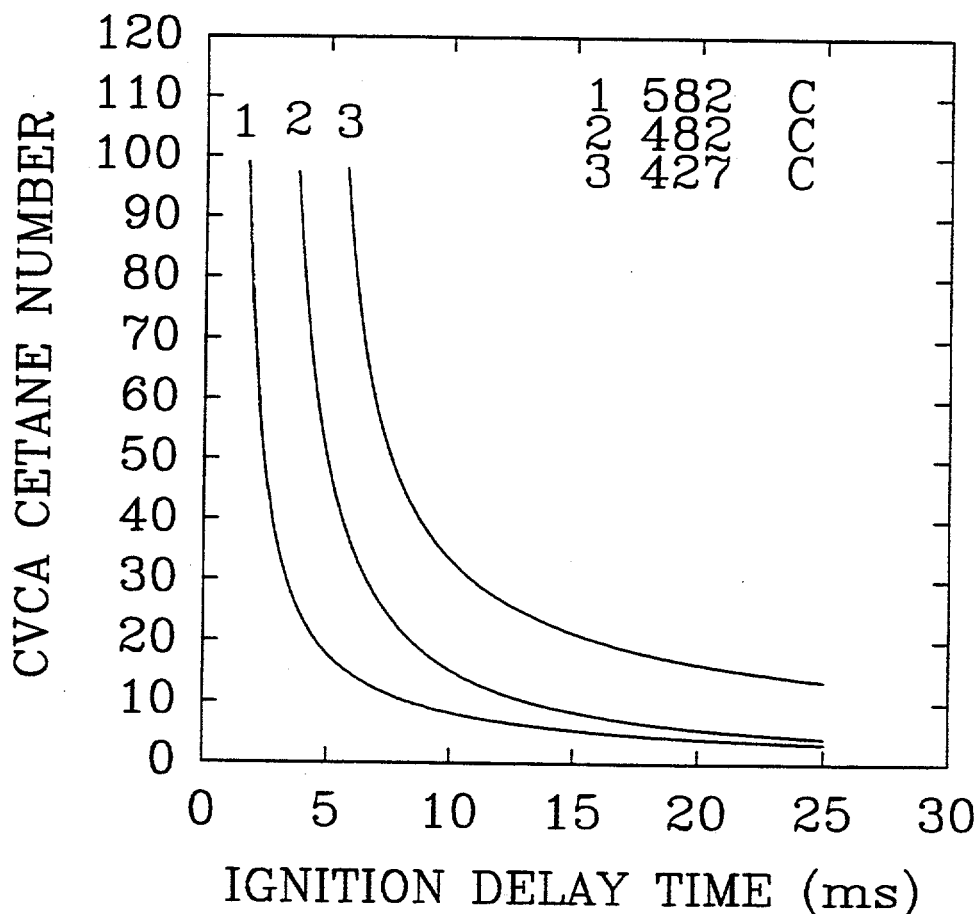

Figure 13. CVCA cetane number calibration curves

24

The experimental results are presented in Table 8 in the form of the ignition delay times and the corresponding cetane numbers for the three test temperatures. Included in Table 8 are the coefficients for the Arrhenius expressions of the ignition delay time as functions of the temperature. The activation energies that are a part of the A2 coefficients in Table 8 are significantly different for some of the materials, but are very similar for most of the materials. The values are in the range of 5 to 15 kcal, somewhat low, relative to other reported ignition values, but within the range of data obtained earlier with this apparatus Ryan et al., 1988; Siebers, 1985; Spadaccini et al., 1983).

Figure 14 is a bar chart showing the cetane ratings of each fraction for three light cycle oils at 582°C. The indicated cetane numbers of the light-cycle oils are low, but the addition of hydrogen causes the CN to increase somewhat in going to the low-sulfur material, and even more in the more severely processed low-aromatic material. Also, the cetane number is a function of the boiling point of the material. This is shown clearly in Figure 14 by the fact that cetane rating of the lower boiling fractions are all similar and the ratings of the heavier fractions are higher. The results for the other materials are similar, but the relationship between cetane number and the boiling point is not as pronounced for the light-coker gas oils and the straight-run diesel fuels. This can be seen by comparing the results for the LCOs in Figure 14 to the corresponding results for the light-coker gas oils in Figure 15 and the straight-run diesel fuels in Figure 16. As seen in Figures 15 and 16, the test temperature also has an effect on the ratings, with the rating generally increasing as the test temperature is reduced.

The cetane rating of the full-boiling materials is a volume-weighted composite of the individual ratings of the fractions. Consequently, the proposed reduction in the end-point specification of diesel fuels for particulate emission control will apparently have an adverse affect on the overall cetane number of the fuel, and possibly have a corresponding adverse effect on the NOx emissions.

Addition of hydrogen to the feedstock has the effect of increasing the cetane number, as shown for the LCOs in Figure 14. The cetane rating trends upward in going from the feedstock to the processed materials. The 582°C test condition shows in Figure 14 that the effects of hydrogenation are more dominant in the higher boiling fractions. These trends are also more apparent at the lower test temperatures, as shown in Figures 14 to 16. These results also suggest that the proposed reduction in end point will have an adverse impact on the cetane number for the same level of hydrotreatment as the lower boiling ranges.

The light-coker gas oils all had higher cetane ratings than the corresponding light-cycle oils, as seen by comparing the results in Figure 14 to those in Figure 17. While there is a trend for concentration of the cetane rating in the higher boiling fractions, this trend is not as strong as for the light-cycle oils. In addition, it appears that the effects of hydrogenation are reduced; they are more uniformly distributed over the boiling range; and, they show less of an effect arising from test temperature than for the light-cycle oils.

Figure 18 presents the results for the straight-run diesel fuels at the 582°C test temperature. The cetane rating is distributed over the boiling range and is a function of the test temperature, with a general upward trend as the test temperature is decreased. The addition of hydrogen appears to have little effect on the cetane number of the materials. If there is a trend for hydrogenation severity, it appears to be one of *reduced* cetane number.

The relationships between cetane number and aromatics content are shown in Figure 19 for the three feedstocks used in this work. The cetane number appears linearly related to the aromatics content, at least for the specific samples used in this work. The intercepts of the two blendstocks are similar to each other

Sample Name	ID No.	@ 582°C (ms)	CN @ 582°C	@ 582°C (ms)	CN @ 482°C	@ 426°C (ms)	CN @ 426°C	Ln (A1)	A1	A2
LCO	FL-1538	6.2	15.5	9.0	18.6	14.2	21.6	-0.5	0.6	1315
FRAC. 1	FL-1555	6.3	15.2	12.2	11.9	23.8	11.0	-1.8	0.2	2105
FRAC. 2	FL-1556	6.6	17.0	10.8	14.3	16.2	18.1	-1.2	0.3	1692
FRAC. 3	FL-1557	-	-	-	-	-	-	-	-	-
FRAC. 4	FL-1558	6.9	13.9	11.2	13.5	24.9	10.4	-1.6	0.2	2009
FRAC. 5	FL-1559	6.2	15.6	10.6	14.7	18.1	15.6	-1.1	0.3	1708
FRAC. 6	FL-1560	5.9	16.3	9.5	6.6	14.7	20.6	-0.7	0.5	1452
FRAC. 7	FL-1561	5.0	19.1	8.1	22.2	16.0	18.4	-1.6	0.2	1821
LSLCO	FL-1615	5.4	17.9	8.1	20.5	11.2	30.4	-0.3	1.3	892
FRAC. 1	FL-1850	6.9	14.0	11.0	13.1	18.6	12.3	-0.9	0.4	1575
FRAC. 2	FL-1851	6.2	15.4	10.5	14.3	17.6	16.2	-1.0	0.4	1650
FRAC. 3	FL-1852	6.1	15.7	11.1	13.3	16.1	18.1	-0.9	0.4	1557
FRAC. 4	FL-1853	5.6	17.3	9.5	16.9	15.0	20.1	-1.0	0.4	1584
FRAC. 5	FL-1854	5.1	18.6	7.4	25.2	11.8	28.2	-0.7	0.5	1318
FRAC. 6	FL-1855	5.0	19.9	9.5	16.7	14.2	21.0	-1.3	0.3	1688
FRAC. 7	FL-1856	-	-	6.9	38.1	9.7	37.8	-	-	-
LALCO	FL-1562	2.8	38.4	5.7	37.9	7.6	57.0	-1.7	0.2	1616
FRAC. 0	FL-1566	4.4	22.4	7.0	27.0	10.5	33.5	-0.9	0.4	1402
FRAC. 1	FL-1567	4.0	24.5	4.7	30.5	9.2	41.5	-0.9	0.4	1276
FRAC. 2	FL-1568	3.4	30.1	6.0	36.3	9.0	43.2	-1.5	0.2	1558
FRAC. 3	FL-1569	3.3	31.4	6.3	32.9	9.2	41.7	-1.6	0.2	1654
FRAC. 4	FL-1570	2.8	39.6	5.7	39.9	8.7	45.0	-2.1	0.1	1848
FRAC. 5	FL-1571	2.6	42.1	5.6	41.1	7.9	53.5	-2.0	0.1	1767
FRAC. 6	FL-1572	1.9	77.2	4.2	74.3	6.3	83.4	-2.6	0.1	1926

Table 8. Ignition Delay Times, CVCA Cetane Numbers, and Arrhenius Coefficients
For Delay (ms) = $A_1 \exp (A_2/T)$
(continued)

Sample Name	ID No.	@ 582°C (ms)	CN @ 582°C	@ 582°C (ms)	CN @ 482°C	@ 426°C (ms)	CN @ 426°C	Ln (A1)	A1	A2
LCGO	FL-1440	3.5	29.0	6.1	35.1	9.2	41.2	-1.4	0.2	1555
FRAC. 1	FL-1546	3.9	25.6	6.4	32.4	9.0	42.8	-1.0	0.4	1355
FRAC. 2	FL-1547	3.6	27.9	6.0	.36.5	9.0	42.6	-1.2	0.3	1469
FRAC. 3	FL-1548	3.4	30.1	6.6	30.6	9.8	37.1	-1.7	0.2	1715
FRAC. 4	FL-1549	3.5	29.1	6.9	28.4	8.7	45.4	-1.3	0.3	1490
FRAC. 5	FL-1550	3.2	32.8	6.3	32.8	8.5	47.2	-1.6	0.2	1598
FRAC. 6	FL-1551	3.2	31.7	6.1	34.9	8.3	48.6	-1.4	0.2	1524
LSLCGO	FL-1442	3.1	33.3	5.9	37.0	9.2	41.5	-1.8	0.2	1726
FRAC. 0	FL-1862	3.6	28.2	6.3	33.6	10.6	33.1	-1.7	0.2	1734
FRAC. 1	FL-1863	3.4	29.5	6.4	32.5	9.4	39.8	-1.5	0.2	1618
FRAC. 2	FL-1864	3.5	29.2	6.1	35.3	8.8	44.1	-1.3	0.3	1502
FRAC. 3	FL-1865	3.4	30.4	6.5	31.3	7.7	56.1	-1.0	0.4	1348
FRAC. 4	FL-1866	3.1	33.7	6.3	32.9	8.6	46.3	-1.7	0.2	1651
FRAC. 5	FL-1867	2.8	37.8	5.8	38.6	7.5	59.3	-1.6	0.2	1564
LALCGO	FL-1443	2.9	37.7	5.6	42.2	8.3	49.4	-1.9	0.2	1710
FRAC. 0	FL-1597	3.6	28.2	6.8	28.9	11.7	28.5	-2.0	0.1	1887
FRAC. 1	FL-1598	3.3	30.5	6.1	34.8	9.3	40.4	-1.6	0.2	1642
FRAC. 2	FL-1599	3.2	31.7	5.8	38.0	8.3	48.7	-1.4	0.2	1515
FRAC. 3	FL-1600	3.1	33.7	5.7	39.8	8.2	50.6	-1.5	0.2	1557
FRAC. 4	FL-1601	2.8	39.0	5.7	39.2	7.9	53.7	-1.8	0.2	1681
FRAC. 5	FL-1602	2.6	44.1	5.3	45.7	6.7	72.2	-1.7	0.2	1564
FRAC. 6	FL-1603	2.2	54.9	4.9	39.2	7.2	62.6	-2.4	0.1	1887
SRD	FL-1627	2.2	56.2	5.3	45.9	7.5	58.6	-2.6	0.1	1976
FRAC. 1	FL-1793	3.1	33.9	5.8	37.9	8.9	43.4	-1.8	0.2	1705
FRAC. 2	FL-1794	2.7	41.1	4.3	70.8	8.0	52.6	-2.0	0.1	1717
FRAC. 3	FL-1795	2.7	40.5	5.3	45.6	7.6	58.8	-1.8	0.2	1664

Table 8. Ignition Delay Times, CVCA Cetane Numbers, and Arrhenius Coefficients
For Delay (ms) = $A_1 \exp(A_2/T)$
(continued)

Sample Name	ID No.	@ 582°C (ms)	CN @ 582°C	@ 582°C (ms)	CN @ 482°C	@ 426°C (ms)	CN @ 426°C	Ln (A1)	A1	A2
FRAC. 4	FL-1796	2.6	42.5	5.3	44.6	7.8	54.6	-2.0	0.1	175
FRAC. 5	FL-1797	2.5	45.1	4.7	56.5	7.3	61.8	-2.0	0.1	169
FRAC. 6	FL-1798	2.1	64.2	4.5	62.0	6.8	70.0	-2.6	0.1	192
FRAC. 7	FL-1799	-	-	4.5	60.3	6.2	84.0	-	-	-
LASRD	FL-1873	2.1	61.3	5.0	51.6	7.0	66.2	-2.5	0.07	194
FRAC. 0	FL-1876	4.2	23.1	7.6	24.5	12.7	25.3	-1.6	0.2	174
FRAC. 1	FL-1877	3.2	31.7	6.0	36.4	9.4	40.2	-1.7	0.2	169
FRAC. 2	FL-1878	2.8	38.6	5.7	39.4	7.4	59.9	-1.6	0.2	157
FRAC. 3	FL-1879	2.6	44.3	5.5	41.9	8.0	51.9	-2.2	0.1	184
FRAC. 4	FL-1880	2.4	48.8	5.0	50.8	7.4	60.6	-2.2	0.1	180
FRAC. 5	FL-1881	2.1	64.2	4.6	60.1	7.2	62.6	-2.7	0.1	201
FRAC. 6	FL-1882	1.9	79.1	4.1	78.0	6.9	68.4	-3.0	0.1	209
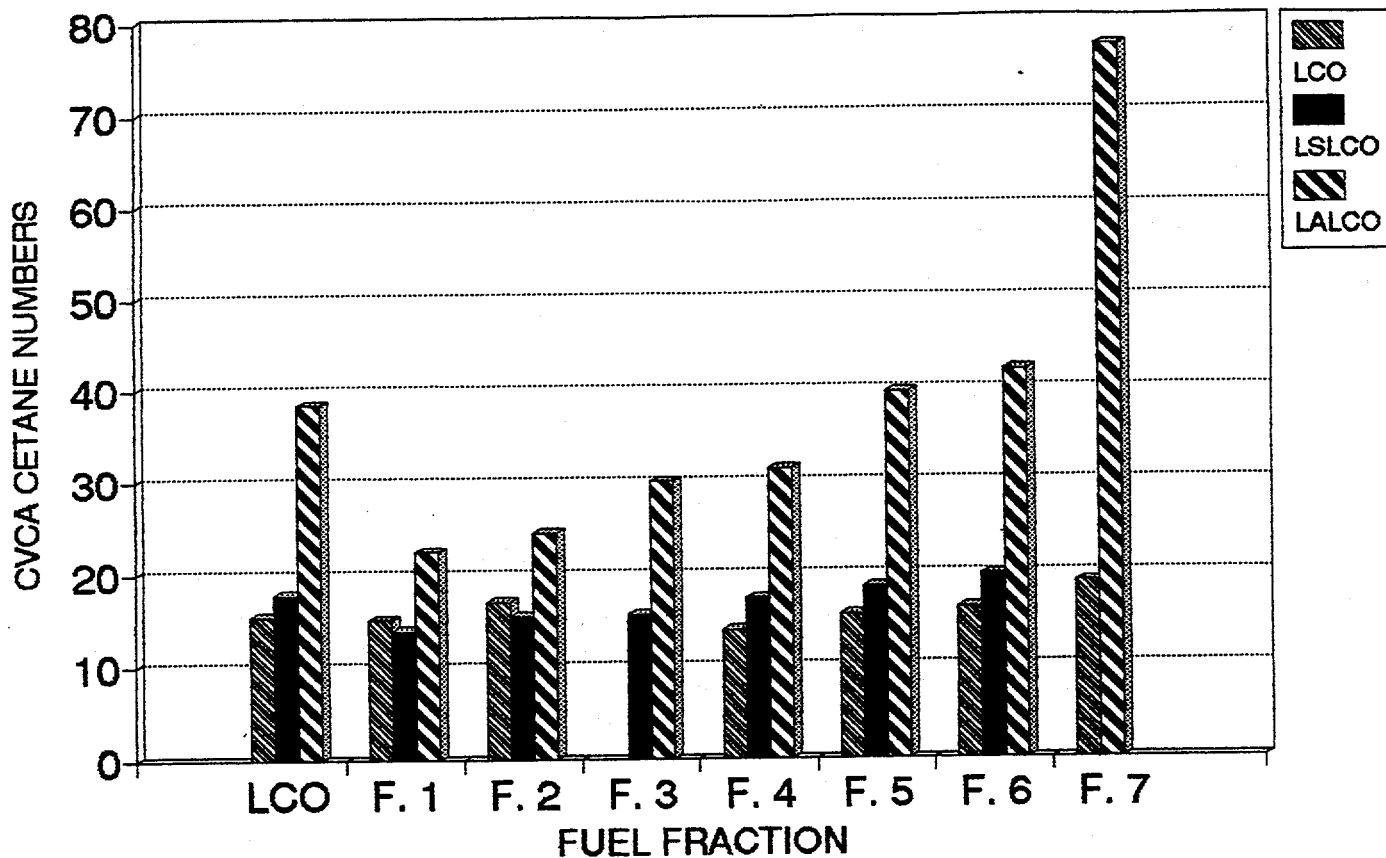
Figure 14. CVCA cetane numbers of LCOs at 582°C
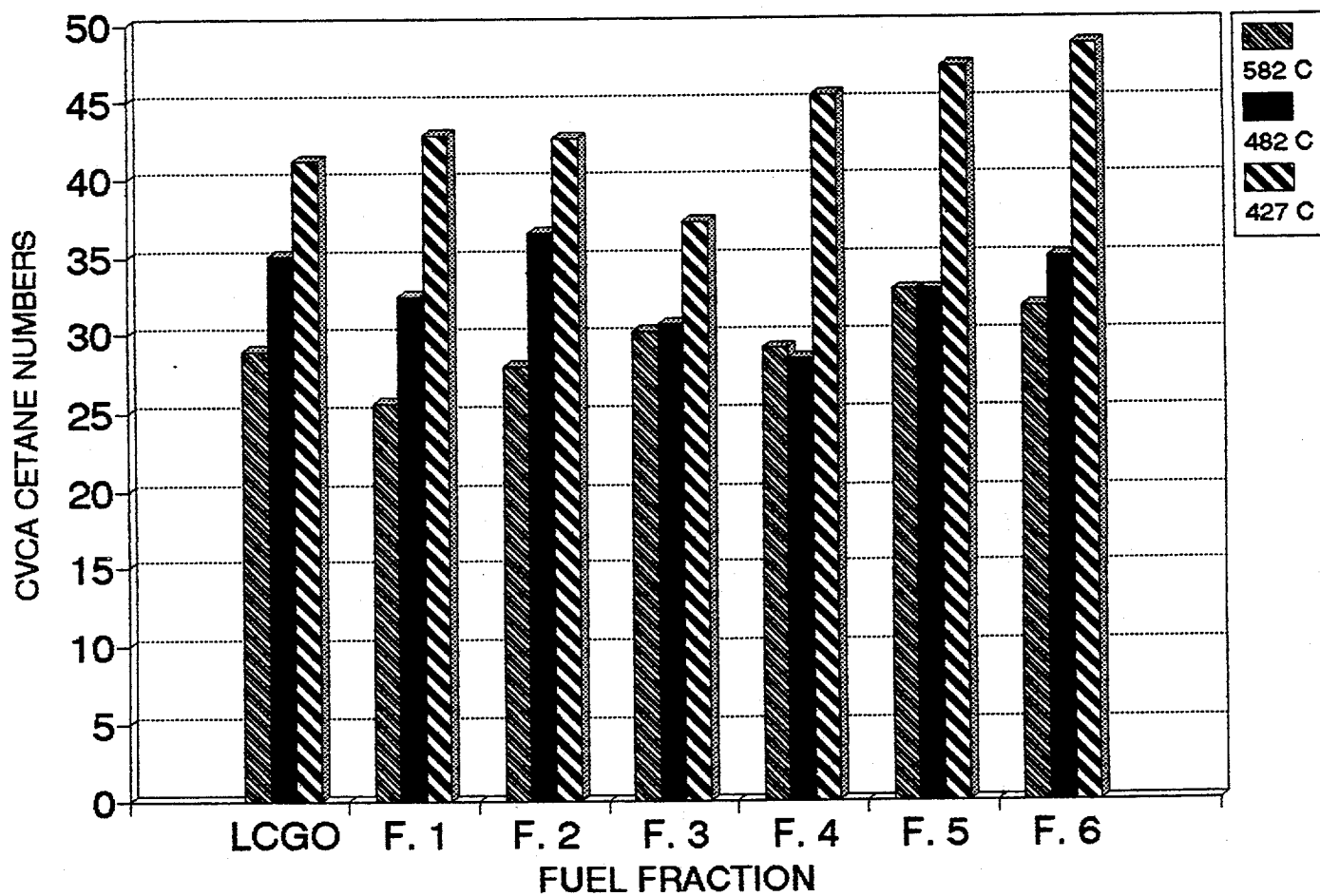
Figure 15. CVCA cetane number of LCGO at three test temperatures

29
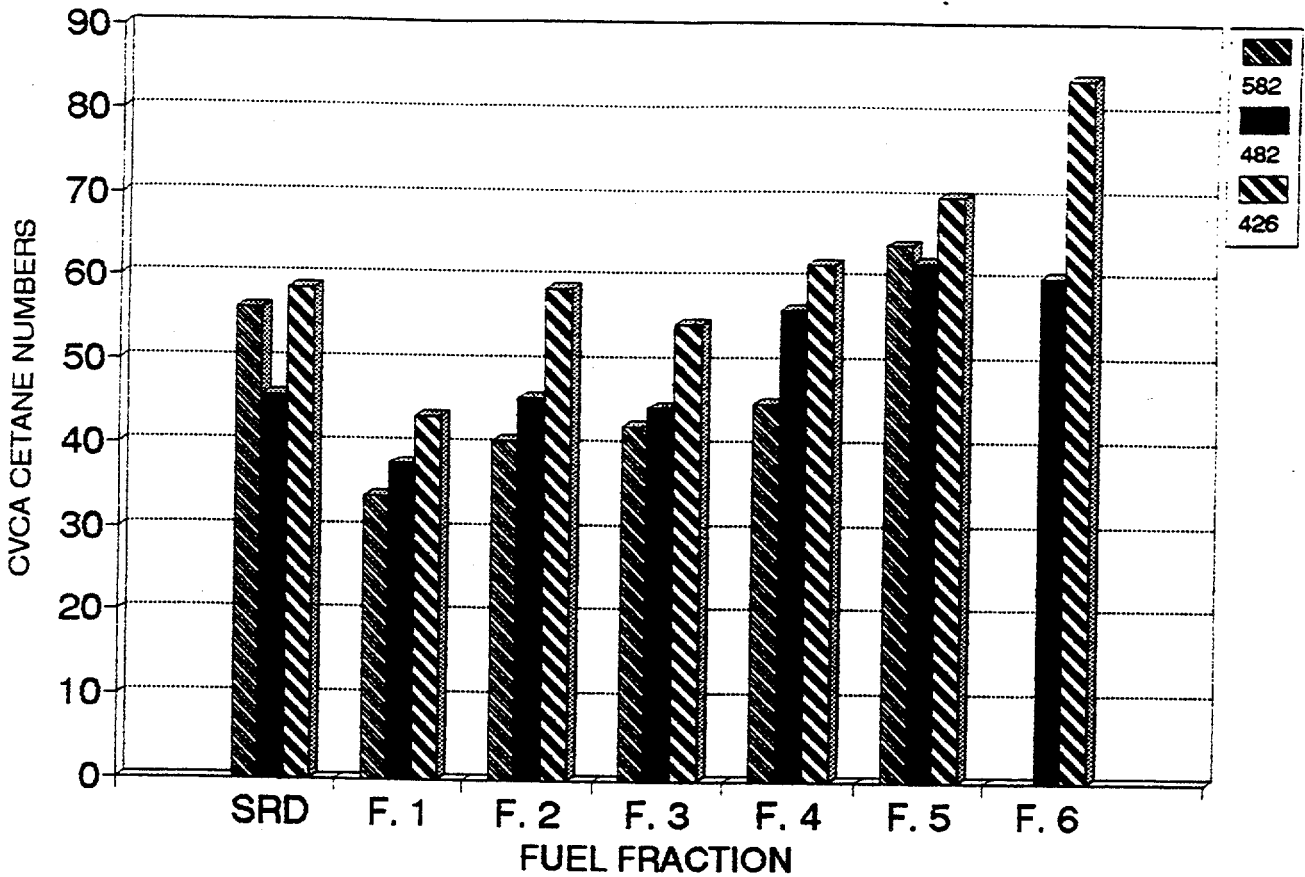
Figure 16. CVCA cetane number of SRD at three test temperatures
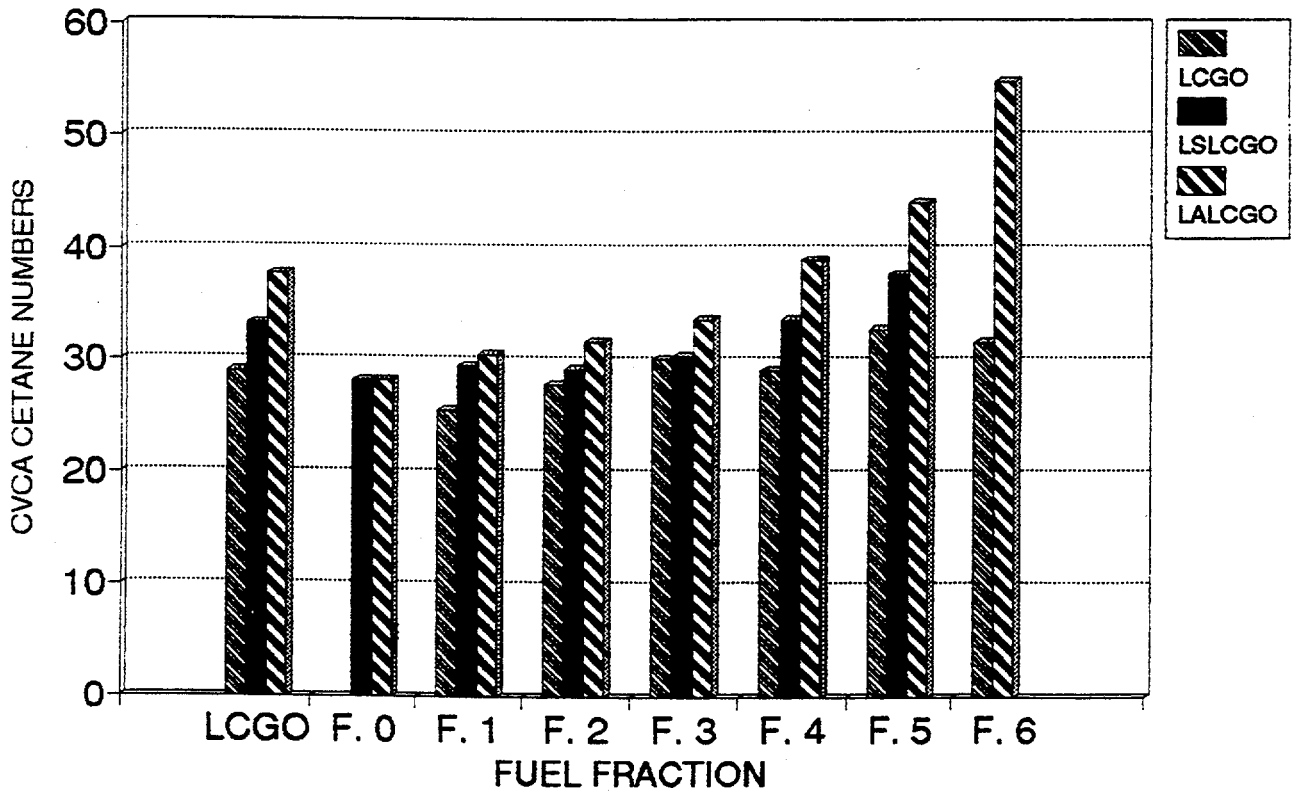
Figure 17. CVCA cetane numbers of LCGOs at 582°C
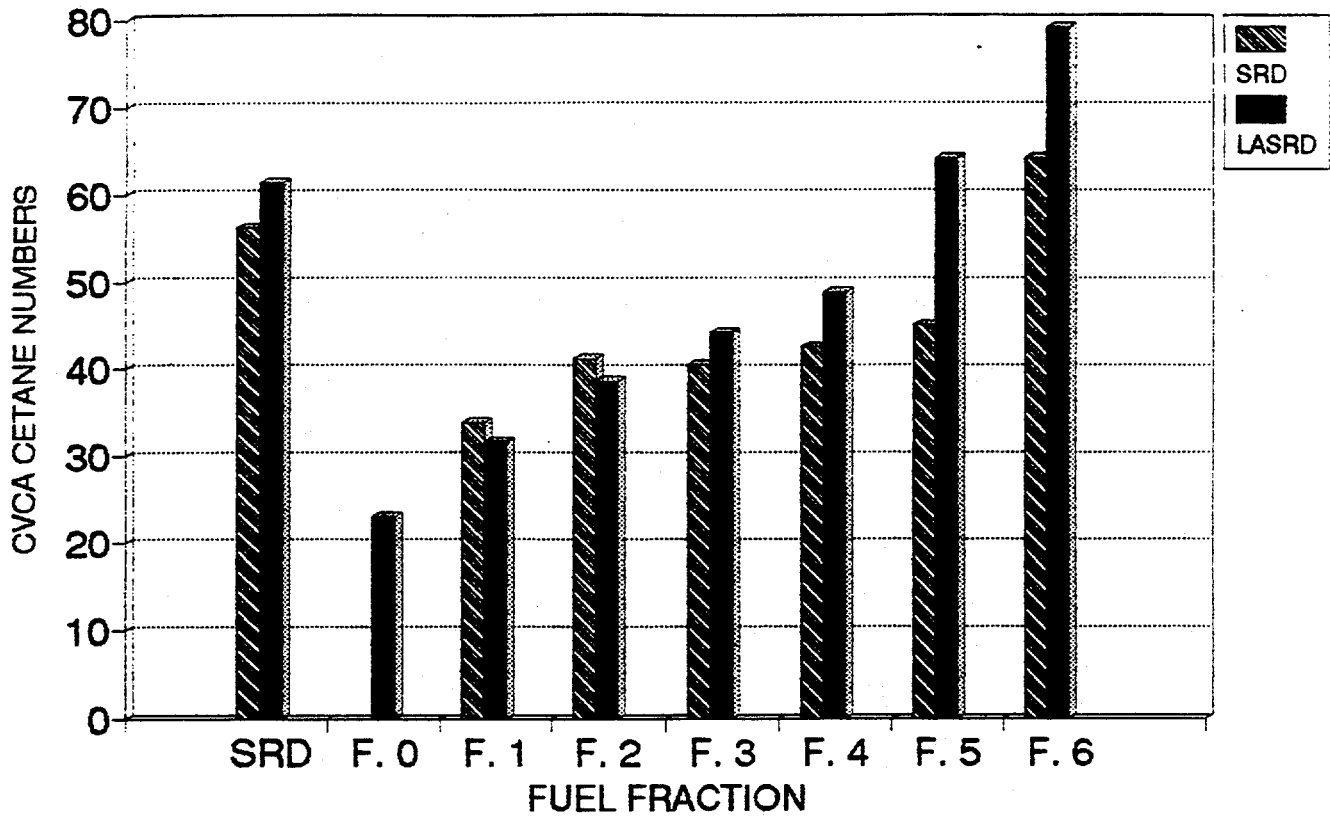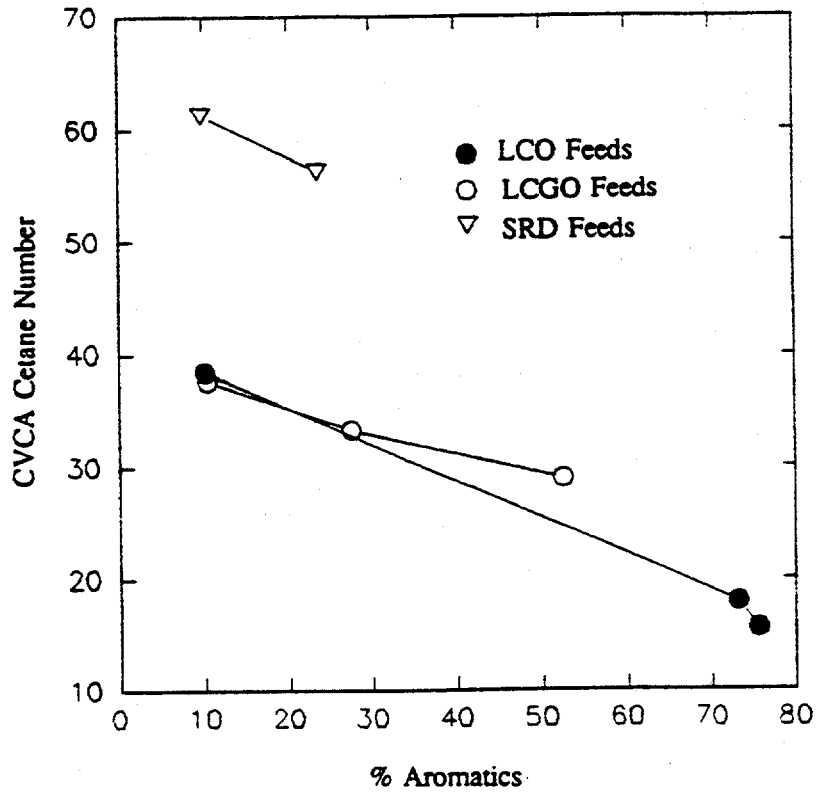
Figure 18. CVCA cetane numbers of SRDs at 582°C

Figure 19. CVCA cetane number versus aromatics for the three feedstocks

31

and significantly different from the straight-run diesel fuel. However, the slopes of all the lines are similar, suggesting that the sensitivity of cetane number to aromatics is uniform for the test materials.

The correlation of CVCA cetane number to the cetane index are presented in Figure 20 for the light-cycle oils and the ASTM D 976 Cetane Index Method. The Index — an empirical correlation developed for fully formulated commercial diesel fuels — is a computed parameter based on the 50% D 86 temperature and the API gravity. As seen in Figure 20, the correlation between the CVCA cetane number and the cetane index is good at the higher cetane numbers, corresponding to the lower aromatic contents that are more typical of the commercial diesel fuels. In addition, the correlation is very good for the straight-run diesel fuels, as shown in Figure 21. These results indicate that it is probably not appropriate to use cetane index for materials that are either higher in aromatic content, or significantly different than the commercial diesel fuels used in the development of the Index.

Engine Ignition Quality

The engine tests were performed in the VCR described earlier in this report, in Appendix B, and by Ryan et al., 1993. The performance and emissions tests were performed at five different test conditions, where the speed and air-fuel ratio (load) were held constant for all of the fuels. The data from these tests were separated and treated in the preliminary analysis as independent experiments. This approach made it possible to examine the fuel effects independent of the normally dominant effects of speed and load.

The complete data set is presented in Appendix A. The results of the ignition quality rating experiments are plotted in Figure 22 as the cetane number determined in the VCR engine versus the cetane number obtained in the CVCA. The important points to note from the comparison presented in Figure 22 are:

1. The data are highly correlated, indicating that both techniques provide consistent indications of the ignition quality of the fuels.

2. The data scatter which increases significantly as the cetane number increases, is associated with defining the start of combustion in the engine at the low compression ratios needed for these fuels. The problem in the CVCA is because the ignition delay times are so short that the normal error represents a larger fraction of the total delay time.

3. The CVCA consistently rates the fuel lower than the engine test. This difference has been observed and reported previously Ryan et al., 1988). The CVCA technique involves calibration using the primary reference fuels, which consists of two pure hydrocarbons. We believe that the difference between the engine and the CVCA is because the CVCA responds to the reference fuels differently than the engine techniques. This difference is manifested by the CVCA consistently displaying two-stage ignition (ignition and slow combustion, followed by an abrupt increase in the combustion rate) on the 15 CN reference fuel. The difference between the engine and the CVCA is consistent and can be accounted for by applying a constant correction factor to the calibration curve.
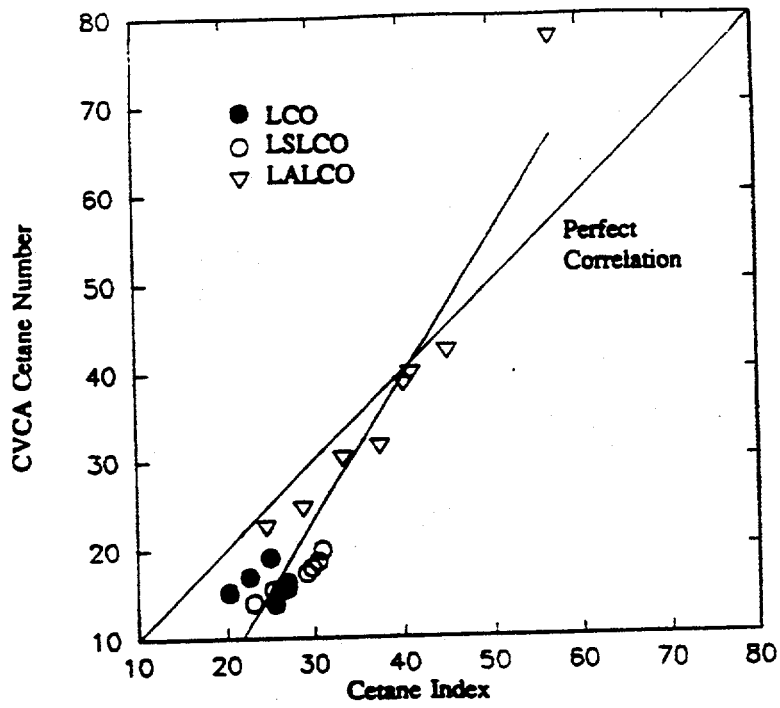
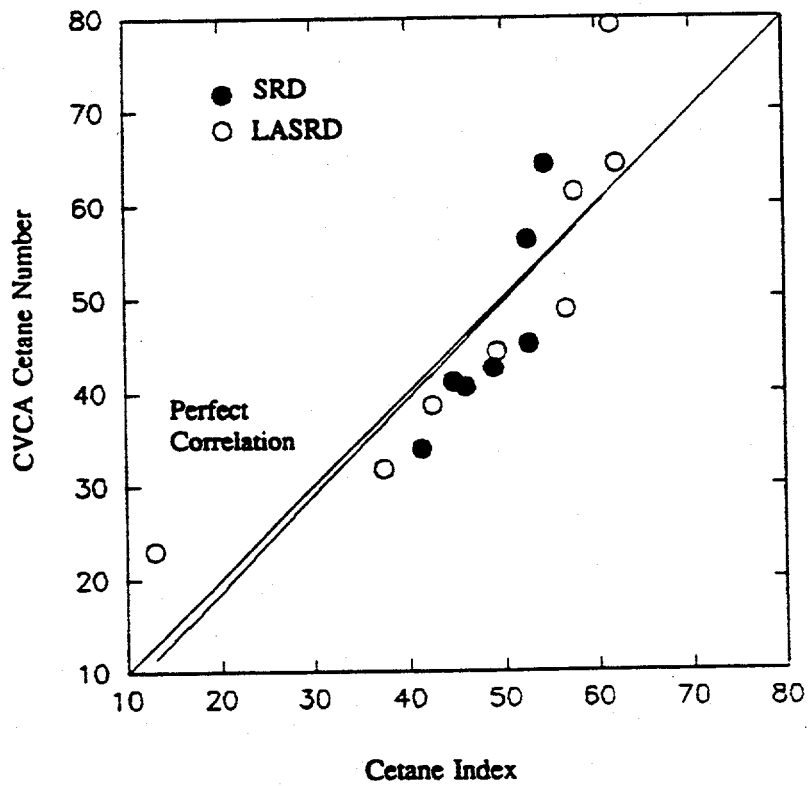Figure 20. CVCA cetane number vs cetane index for the light cycle oils

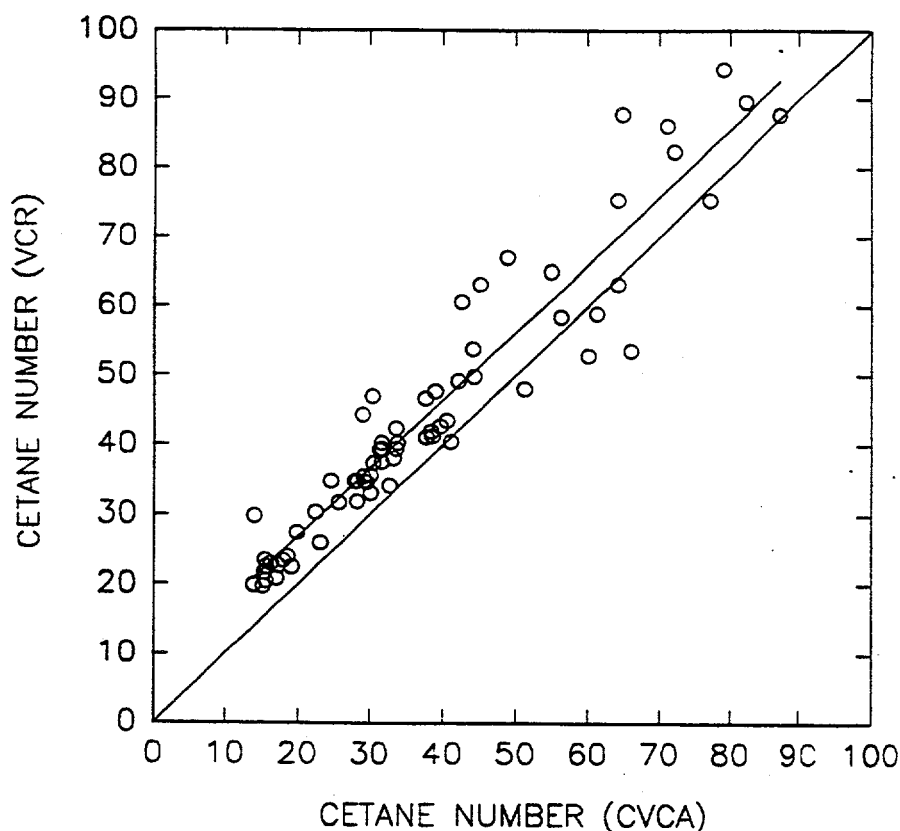Figure 21. CVCA cetane number vs cetane index for the straight run diesel fuels

33

Figure 22. VCR cetane number versus CVCA cetane number

The trends of the VCR engine ratings of the various fuels and fuel fractions are the same as those reported for the CVCA data Ryan et al., 1992). The results for all of the LCO-based fuels are presented in Figure 23. Cetane Number, or ignition quality, is uniformly distributed across the boiling range of the base material. Hydrotreating to the low-sulfur level had only minor impact on the cetane number, mainly in the higher boiling point fractions. Hydrotreating to the low-aromatic level, however, had a significant effect on the cetane number of all fractions; again, hydrotreating was most effective in increasing the cetane number of the higher boiling point fractions. Based on the corresponding data on aromatic content, it is clear that the sulfur reduction was accomplished with very little consumption of hydrogen. It also appears that the heavier fractions consume more hydrogen than the lighter fractions.

The light coker gas oil (LCGO) data are presented in Figure 24. The results are very similar to those of the LCOs, with a uniform distribution of cetane number across the boiling range for the base material. The one exception is that cetane numbers of all of the fractions are higher than those of the corresponding LCOs. The aromatic content of these materials are lower than the aromatic content of the LCOs, and hydrotreating apparently produces a more-uniform effect on reducing the aromatic content and increasing the cetane number across the boiling range. Hydrotreating does, however, have a more pronounced effect on increasing the cetane number of the heavier fractions. Similar results for cetane index were given in Figure 12.

The results for the straight-run diesel (SRD) fuel and the Fischer-Tropsch (F-T) distillate are presented in Figure 25. The cetane number of these materials are higher than the other components, and all three have a high proportion of the cetane number concentrated in the higher boiling-point fractions. Because the sulfur content of the SRD was already very low, hydrotreating was used only to reduce the aromatic content of the fuel. Similar to the other fuels, the processing was more effective in increasing the cetane number of the heavier fractions. The F-T distillate, already a highly processed material, had effectively no sulfur or aromatics and was not further processed in this project.
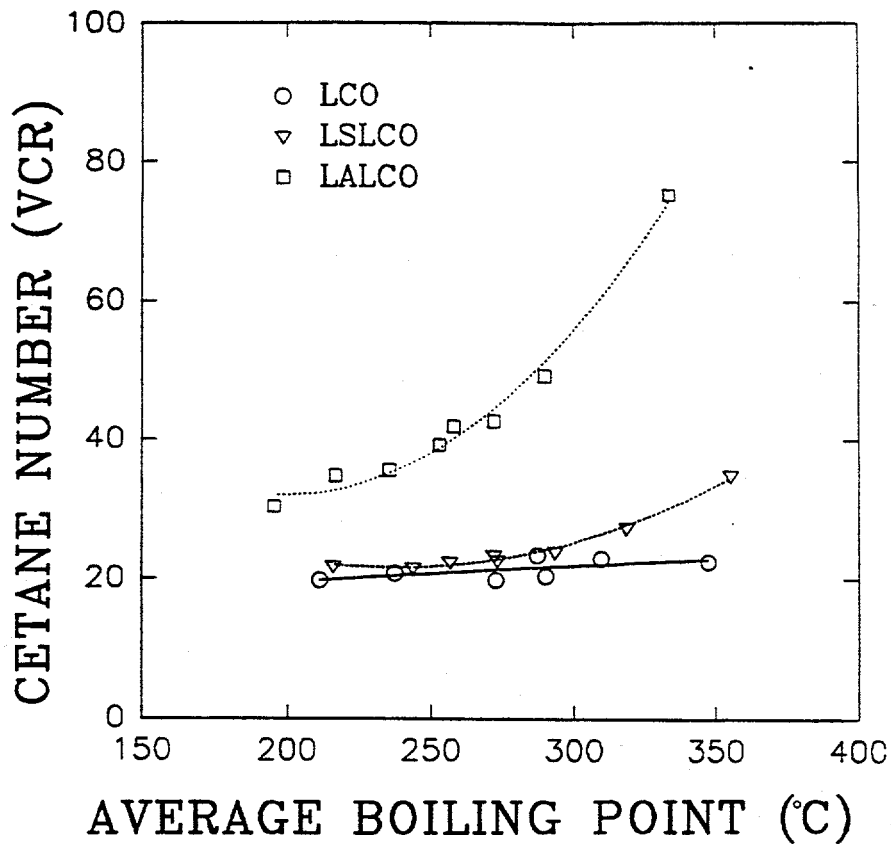
34

Figure 23. Cetane number (VCR) versus the average boiling point for the light-cycle oil
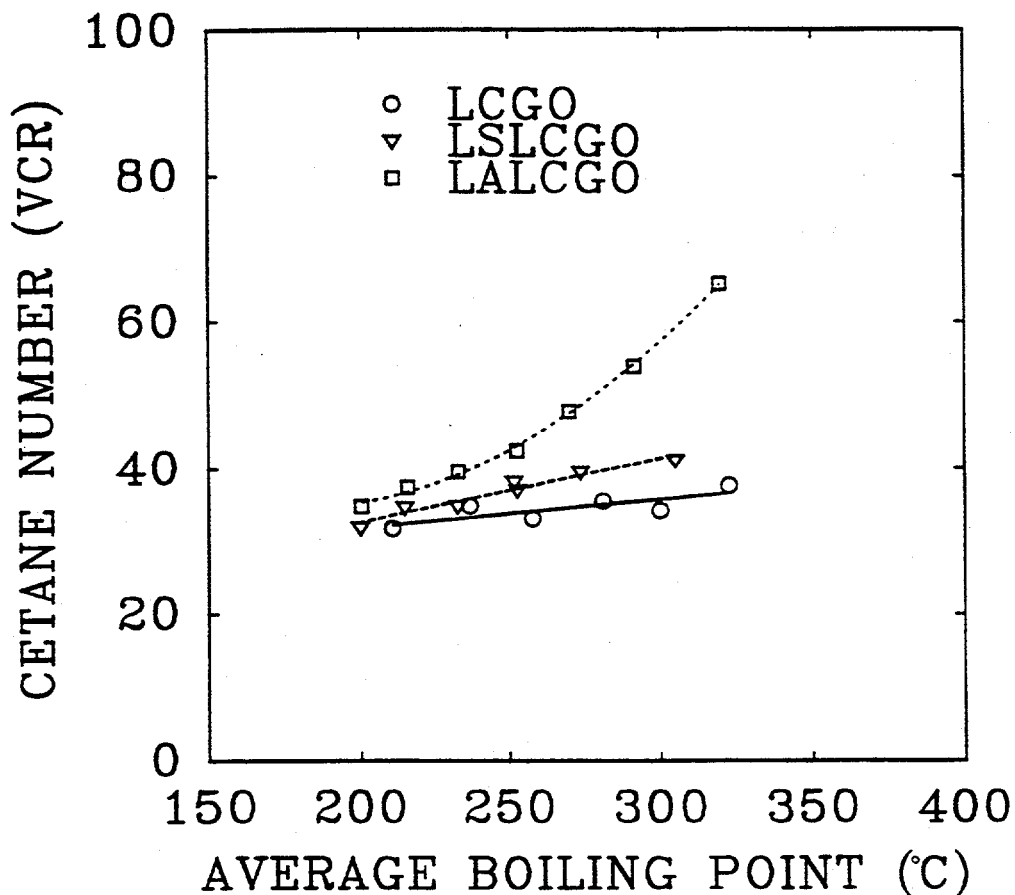

Figure 24. Cetane number (VCR) versus average boiling point for the light-coker gas oil
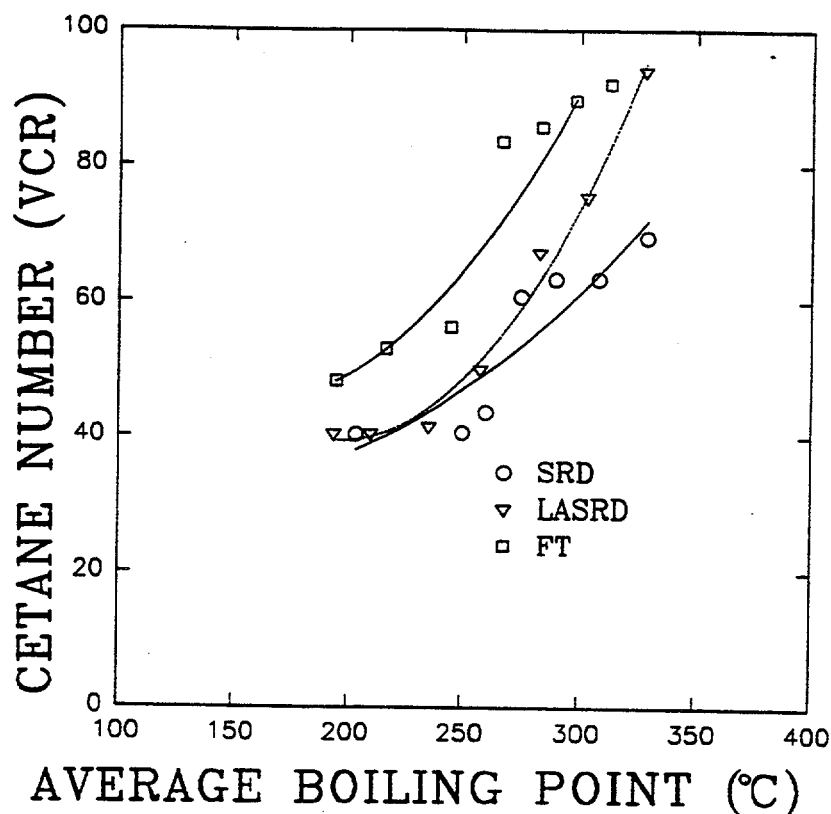
Figure 25. Cetane number versus the average boiling point for the straight-run diesel fuels and Fischer-Tropsch fuels

These results indicate that, while hydrotreating has a nearly uniform effect in reducing the aromatic content across the boiling range, it is more effective in increasing the cetane number of the heavier fractions. Consistent with the results of the CVCA measurements, hydroprocessing apparently not only reduces the aromatics content, but also produces materials in these heavier fractions that have much higher cetane number than the products appearing in the lighter fractions.

Preliminary stepwise regression analysis of the VCR results indicated that 89% of the variation in the cetane number in the test fuel matrix can be accounted for by using only the average boiling point and the specific gravity. The analysis also indicated that wt% carbon and concentration of alkyl groups associated with aromatic rings were directly related to the cetane number.(12) These relationships are reflected in the final regression equation:

$$CN = A_1 + A_2 \times (\text{Alkylbenzenes}) + A_3 \times (\text{T50\%})$$
$$+ A_4 \times (\text{Indenes}) + A_5 \times (\text{Paraffins})$$
$$+ A_6 \times (\text{Specific Gravity}) + A_7 \times (\text{Viscosity@40°C})$$

where the concentrations are in wt%, specific gravity is in gM/mL, viscosity is in centistokes (cSt), and where:

A_1 =	277.1			R^2 =	0.94
A_2 =	0.54	A_5 =	− 0.13		
A_3 =	0.31	A_6 =	− 437.3		
A_4 =	− 1.83	A_7 =	− 1.98		

36

The direct relationship between the cetane number and the aromatic associated alkyl groups and boiling point information is consistent with the preliminary analysis. The inverse relationship with the viscosity is probably related to the effect on fuel atomization and evaporation, and the resulting influence on the physical aspects of the ignition delay time. The specific gravity effect is consistent with previous findings, as reflected in the correlations used to compute cetane index. The inverse relationship with the indenes is consistent with the fact that indenes have *relatively* high octane numbers, high autoignition temperature, and correspondingly low cetane number.

The inverse relationship with the paraffins, however, is somewhat surprising in that the autoignition temperatures of the paraffins are generally low, and the corresponding cetane numbers are high relative to the aromatic materials. This relationship is reflected in the numerically small coefficient of the paraffin term, $A_5 = ^-0.13$, in the cetane number equation. The inclusion of the paraffins may possibly account for the fact that hydroprocessing did not result in an increase in the paraffins in all cases; most noticeably, the light-cycle oil as multicyclics were converted to monocyclics and were still aromatic. Hydroprocessing did, however, always increase the cetane number of the products, due to the increases in higher-cetane-number compounds, including paraffins and cycloparaffins. The conversion process and the distribution of products is dependent on the composition of the feedstock.

The effect of boiling range for the straight-run diesel (SRD) fuel and the Fischer-Tropsch (F-T) distillate are presented in Figure 26. The cetane numbers of these materials are higher than the other components and all three have a high proportion of the cetane number concentrated in the higher boiling-point fractions. Because the sulfur content of the SRD was already very low, hydrotreating was used only to reduce the aromatic content of the fuel. Similar to the other fuels, the processing was more effective in increasing the cetane number of the heavier fractions.
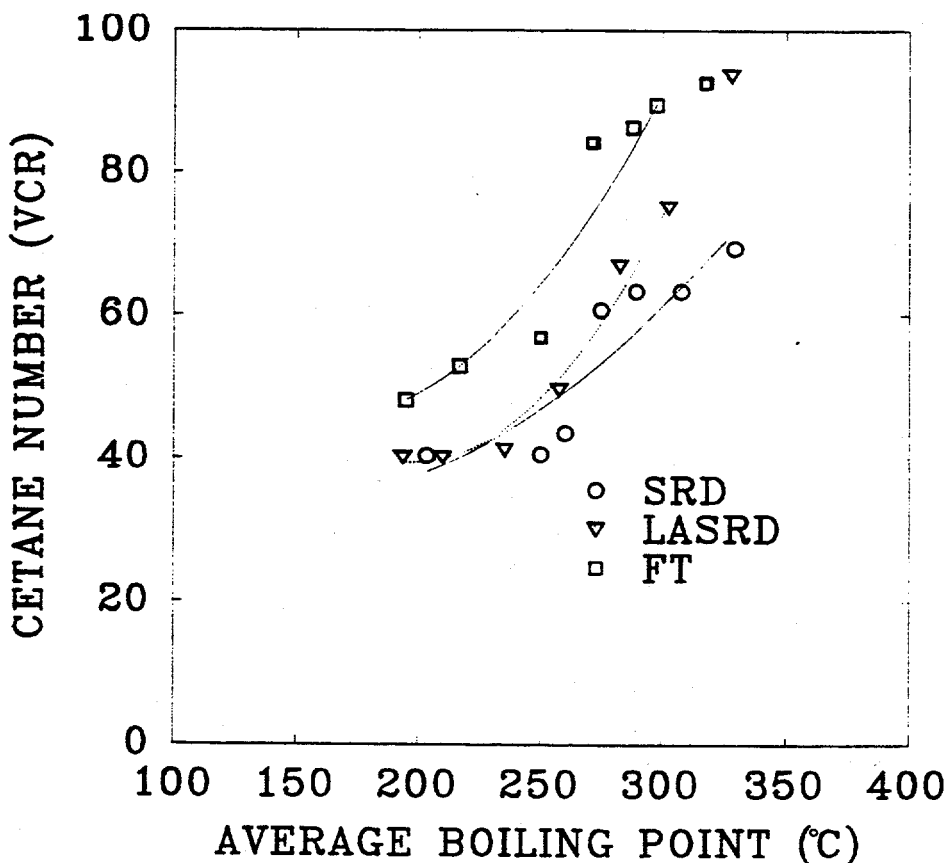

Figure 26. Effect of hydrogenation by boiling range

37

Of particular interest is the value of F-T distillate as a cetane blending stock. We did a blending study in which F-T fuel was blended in different concentrations with each of the three petroleum blendstocks.

The cetane number of these blends based on the CVCA technique is plotted in Figure 27 versus the concentration of the blendstocks in the F-T fuel. The cetane number of blends appears to be a linear function of the concentration for the three materials. While the relationships are essentially linear, the nonlinearity occurs for each material as cetane number decreases:

Sample	Cetane Number of Sample	Max. Deviation of Blend from Linear, %
D-2	32.1	2.1
LCGO	29.2	6.6
LCO	15.9	15.7

This progression tracks the increase in differences in hydrocarbon types between the F-T component and the other three samples. These deviations are small enough to permit an approximation of the cetane number of F-T blends as a linear combination of the volume-weighted values of cetane number for the blend components.
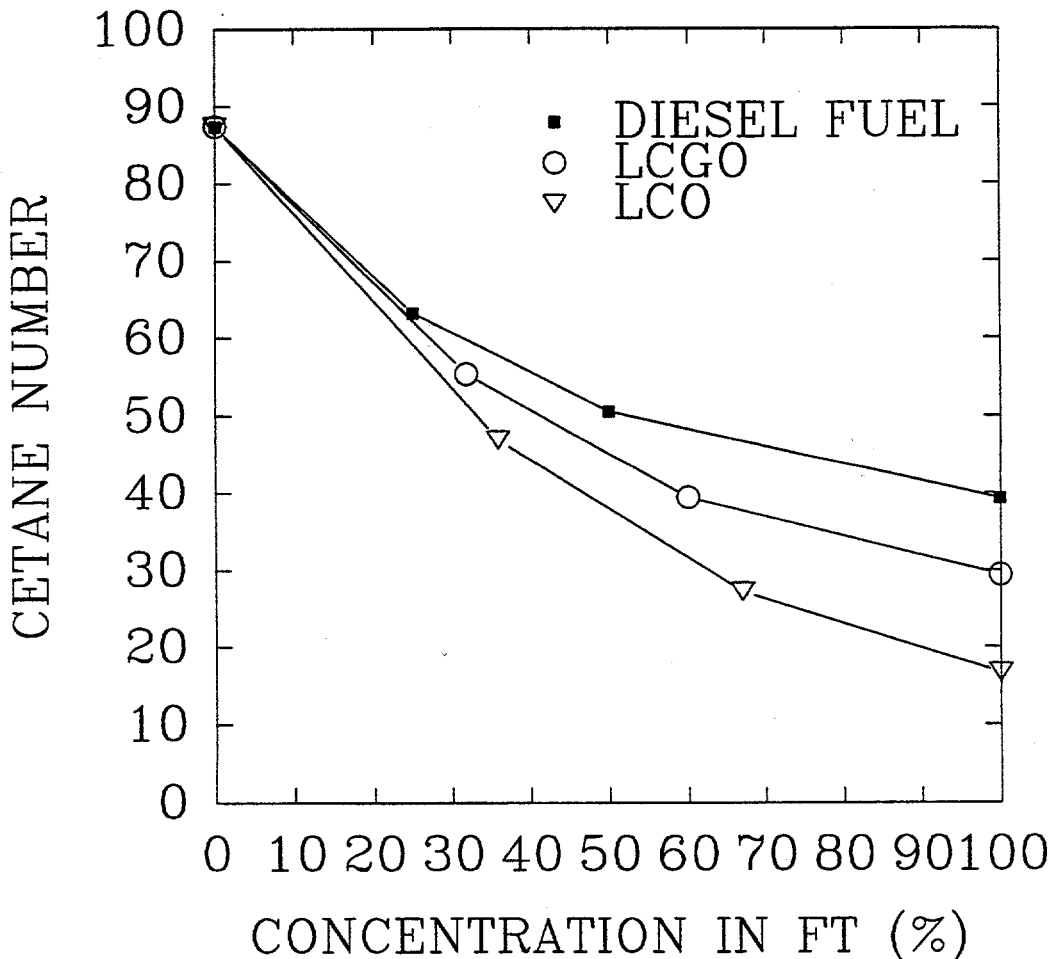

Figure 27. Cetane numbers of blends of F-T distillate with diesel components

38