indicates that the loss of ruthenium signal caused by carbon accumulation over ruthenium is minimal. There was no change in ruthenium surface concentration after the toluene and methylene chloride/methanol extractions, which further indicates that the loss of ruthenium signal by carbon accumulation was minimal.

5.3.5.2.3 NMR Measurements

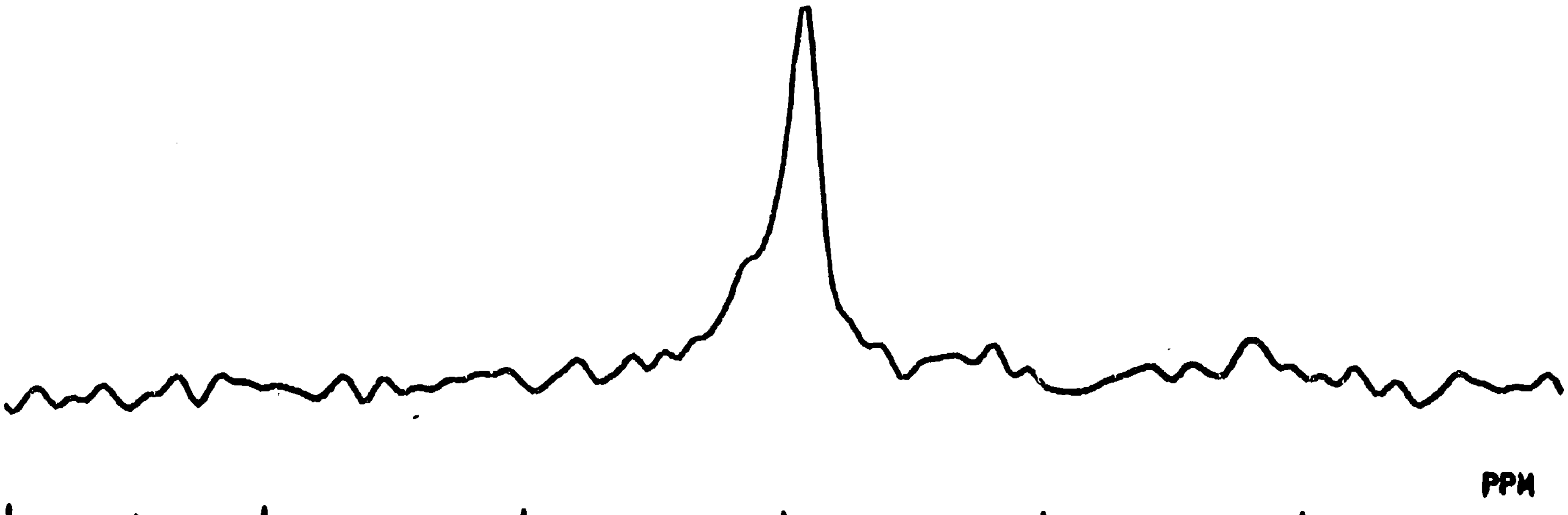
5.3.5.2.3.1 Establishment of Experimental Procedures with Catalyst 4966-124 Tested in Run 39

C13 NMR is a powerful method for analyzing long chain hydrocarbons made by Fischer-Tropsch. The signal pulse block decay (BD) NMR spectra of liquid Fischer-Tropsch waxes consist of a single large peak at 30 ppm from the internal CH_2's, and smaller peaks at 12 (CH_3, terminal α carbon), 29 (CH_2, β carbon), 22 (CH_2, γ carbon) ppm from the terminal groups. The spectra of pure waxes at r temperature in the solid state appear similar to the solution spectra; however, the peaks are broadened, and it is only possible to distinguish two of the terminal group peaks. This indicates that the molecules in the solid wax are mobile enough to average out most of the aniostropic and dipolar interactions which typically lead to peak broadening in the NMR of solids. The ratio of the internal methylene peak to the terminal peaks can be used to estimate the average chain length of the wax.

Magic angle spinning removes peak broadening from anisotropic effects in solids and leads to some peak narrowing for the solid wax spectra. The MSBD (Magic Angle Spinning, Block Decay) spectrum of the Al_2O_3-TiO_2 supported-ruthenium Catalyst 4965-124 after use in Run 39 is shown in Figure 5-323. The used catalyst was soxhlet extracted with n-hexane for seven days, followed by four days extraction with toluene. The single peak observed near 30 ppm can be

Figure 5-323: MSBD C13 NMR SPECTRUM OF PLANT 700 RUN 39 SPENT CATALYST (0-60 ppm), TOLUENE WASHED

NUC: C
NA: 2172
FOBS: 25.200000
FDEC: 100.575000
TLB: 14.994
SW: 400.02 PPM
AL: 1024
DL: 4096
PW1: 6.5 us
CT: 6.00 ms
PD: 2.00 s
FNA: NA700.A01



tentatively assigned to the internal methylene groups in a Fischer-Trospch wax type species retained in the catalyst, despite the soxhlet extracion steps. Peaks from the terminal carbons were not visible. The absence of the terminal groups can be explained by the low signal-to-noise ratio of the spectrum (15:1) and by the long nature of the wax-type molecules which appear to have, on the average, more than 30 carbons.

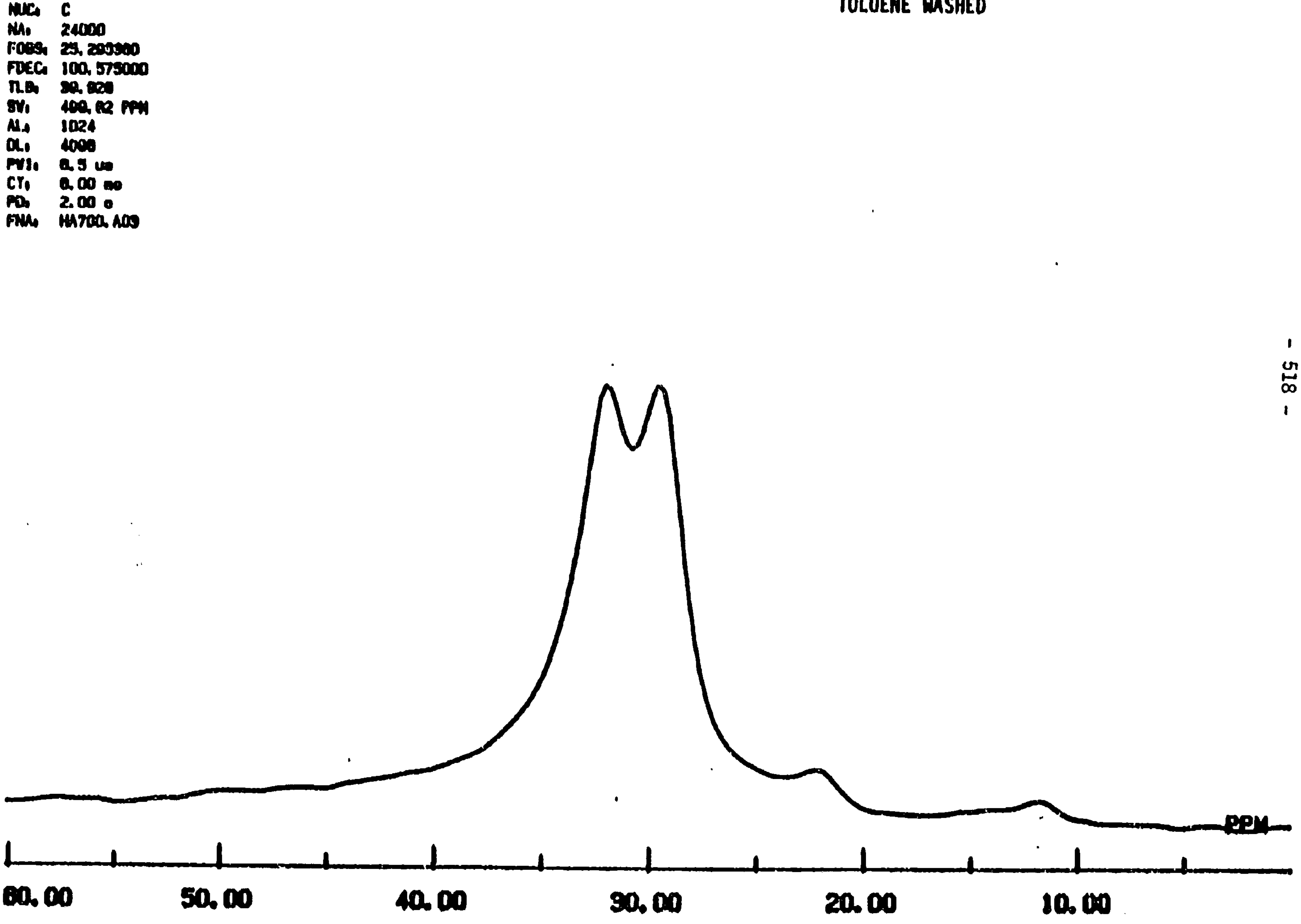
The CPMAS (cross polarization magic angle spinning) spectrum of this sample is shown in Figure 5-324. Cross polarization increases the intensity of resonances from carbons which are in rigid environments. These carbons have long carbon-spin lattice relaxation times and, therefore, the signals from these carbons become saturated when a fast pulse rate of 2 sec. or even 40 sec. is used. Cross polarization enhances the relaxation rates from these rigid carbons which are in the vicinity of hydrogens. At fast relaxation rates the signals do not become saturated and can be observed.

This NMR spectrum shows that, in addition to the peak at 30 ppm, there is now a second peak at 32 ppm. These results indicate that this used ruthenium catalyst had two types of carbons with different restrictions to motion and both of these carbons were hydrocarbon-like.

Further experiments showed that the 32 ppm peak requires less time to build up cross polarization and has a shorter rotating frame relaxation time. These results confirm that there are two types of carbon with different restrictions to motion.

The differences observed here with the two carbon species were reported, in the literature, to exist between crystalline and amorphous polyethylene. Accordingly, the two carbons retained on the catalyst may be associated with hydrocarbon-type compounds having different crystallinity.

Figure 5-324: CPMAS C13 SPECTRUM OF PLANT 700
RUN 39 SPENT CATALYST (0-60 ppm)
TOLUENE WASHED



This CPMAS experiment had 12 times as many scans as the previous MSBD experiment, and therefore, much better signal: noise ratio. This allows the observation of terminal peaks at 12 and 22 ppm. The peak at 22 ppm belongs to the two CH_2 groups at the γ-positions. The height of the 12 ppm terminal Ch_3 peak is at least equivalent to the peak at 22 ppm. This suggests that there are two terminal CH_3 groups in this hydrocarbon-type compound.

It is not presently clear whether these resonances for the terminal groups belong to the more or to the less rigid carbon. Nevertheless, a chain length of about 44 can be calculated from the ratio of the intensity of the terminal peaks to the peak at 32 ppm. If the terminal groups belong both to the more and to the less rigid carbon then the chain length is 100.

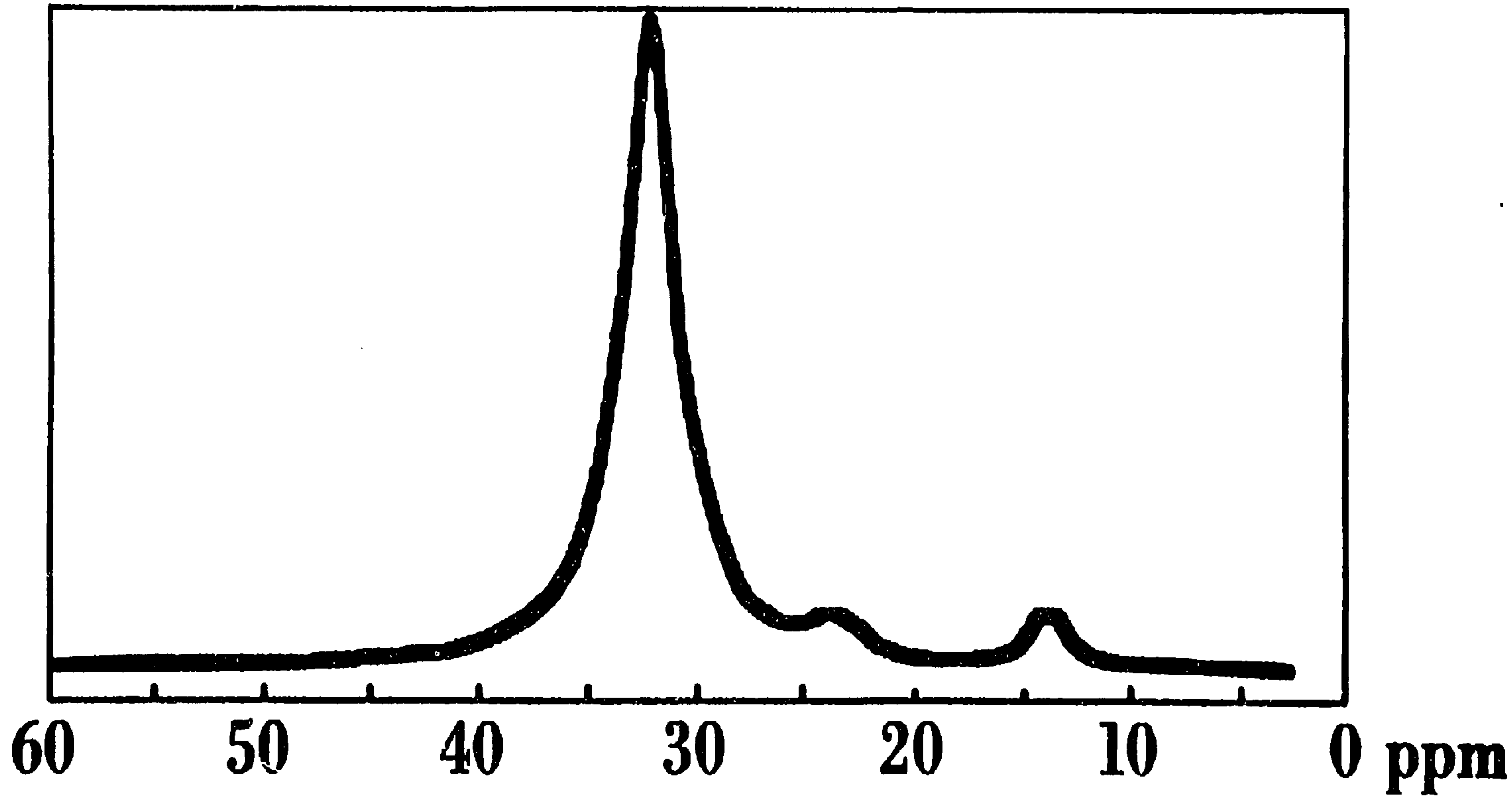
In an attempt to gain further insight as to the nature of the two carbon species, the wax extracted from the used ruthenium catalyst was melted and physically mixed with an unused portion of the ruthenium catalyst.

The CPMAS spectrum had only one peak at about 32 ppm corresponding to the more rigid carbon (Figure 5-325). From the ratio of the peak for the terminal groups to the major peak for the internal CH_2's, a chain length of 26 carbons can be calculated for this sample. This indicates that the carbon retained on the catalyst had much higher molecular weight relative to the wax extracted from the catalyst.

Duncan and Bell *et al.* have previously examined C-13 labeled alkyl intermediates on $Ru-SiO_2$ catalysts by C13 NMR [78,79]. The catalysts they examined were reacted for short periods (minutes) at 190°C. They found that BD spectra of used catalysts which were not exposed to air contained three types of carbon.

Figure 5-325

CPMAS C13 NMR Spectrum of Fresh Ruthenium Catalyst on Alumina-Titania (Mixed with Product Wax)



They assigned these as: α-carbon which was carbidic and associated only with ruthenium, unreactive graphitic carbon, and β-carbon which was hydrocarbon-like. Exposure to air caused the disappearance of the α-carbon. The MSBD spectrum of the air-exposed sample had several peaks from the β-carbon. These were assigned to methylene attached to ruthenium directly or to methylenes attached to ruthenium via other methylene groups as shown in Table 5-55. The reported shifts may differ from those observed in this work because of differences in the method of referencing. The average length of the alkyl substituent appeared to be about 8 carbons.

Table 5-55

C13 NMR Spectral Assignments from Duncan and Bell [78,79]

Peak	Center of Mass	Relative Area	Halfwidth (Hz)	Assignment
(a)	35.1±0.8	0.28±0.06	300	$Ru-\dot{C}H_2-CH_2-$
(b)	28.3±0.2	0.43±0.03	90	$Ru-CH_2-(\dot{C}H_2)_n-CH_2-CH_3$
(c)	21.1±0.1	0.09±0.01	60	$Ru-CH_2-(CH_2)_n-\dot{C}H_2-CH_3$
(d)	18.4±0.1	0.05±0.01	65	$Ru-CH_2-\dot{C}H_2-CH_3$ (?)
(e)	11.7±0.1	0.14±0.01	75	$-\dot{C}H_2-CH_3$

It appears that the carbon species at 30 and 32 ppm observed in this work are not different methylene groups in the same β-type carbon. This is because the amount of the mobile and immobile carbon species are approximately equal. If the 2 ppm shift were caused by different methylene groups in the same hydrocarbon, then the amount of the two carbon species would be significantly different, i.e., only 1 out of 30-40 carbon atoms would be directly attached to ruthenium based on the chain length of hydrocarbons observed and, therefore, would be less mobile.

In order to gain further insight about the nature of the two carbon species, the CPMAS spectra of used Catalyst 4966-124 after soxhlet extraction with cyclohexane, after cyclohexane followed by toluene, and after cyclohexane followed by toluene and methylene chloride/methanol were compared in Figures 5-326, 5-327 and 5-328, respectively. The results show that after cyclohexane extraction the intensity of the peak for the immobile carbon species was higher relative to the mobile species. Both toluene solvent and mixture of methylene chloride/methanol solvents selectively removed the immobile species.

Finally, the region of CPMAS spectra between 100 and 250 ppm for the three samples described above were closely examined and a broad peak was found in each case. (Figure 5-329, shows the results obtained with the fully-extracted samples). Part of this peak was from the probe background, but some of the intensity may be from an aromatic species.

5.3.5.2.3.2 Examination of the Al_2O_3-Supported New Modified Ruthenium Catalyst 4966-180 and the Unmodified Ruthenium Catalyst 4966-198 After Testing in Runs 46 and 47

The CPMAS spectra of the modified and unmodified ruthenium catalysts tested in Runs 46 and 47 are shown in Figures 5-330 and 5-331. The catalyst samples underwent the three soxhlet extraction steps prior to the NMR measurements. The spectra of the two samples were similar. For both samples the peak corresponding to the immobile species was much bigger than the peak corresponding to the mobile species. However, the intensity for the immobile species was higher for the unmodified Catalyst 4966-198.

The spectra of the used catalysts from Runs 46 and 47 had no peaks from the terminal methyls. This is consistent with the failure to observe similar

Figure 5-326 CPMAS C13 Spectrum of Used Al_2O_3-TiO_2 - Supported Ruthenium Catalyst 4966-124 After Soxhlet Extraction with Cyclohexane

NUC: C
NA: 12000
FOBS: 25.203380
FDEC: 100.575000
TLB: 14.934
SW: 490.82 PPM
AL: 1024
DL: 4098
PW1: 0.5 us
CT: 8.00 ms
PD: 2.00 s
FNA: HA700.C01

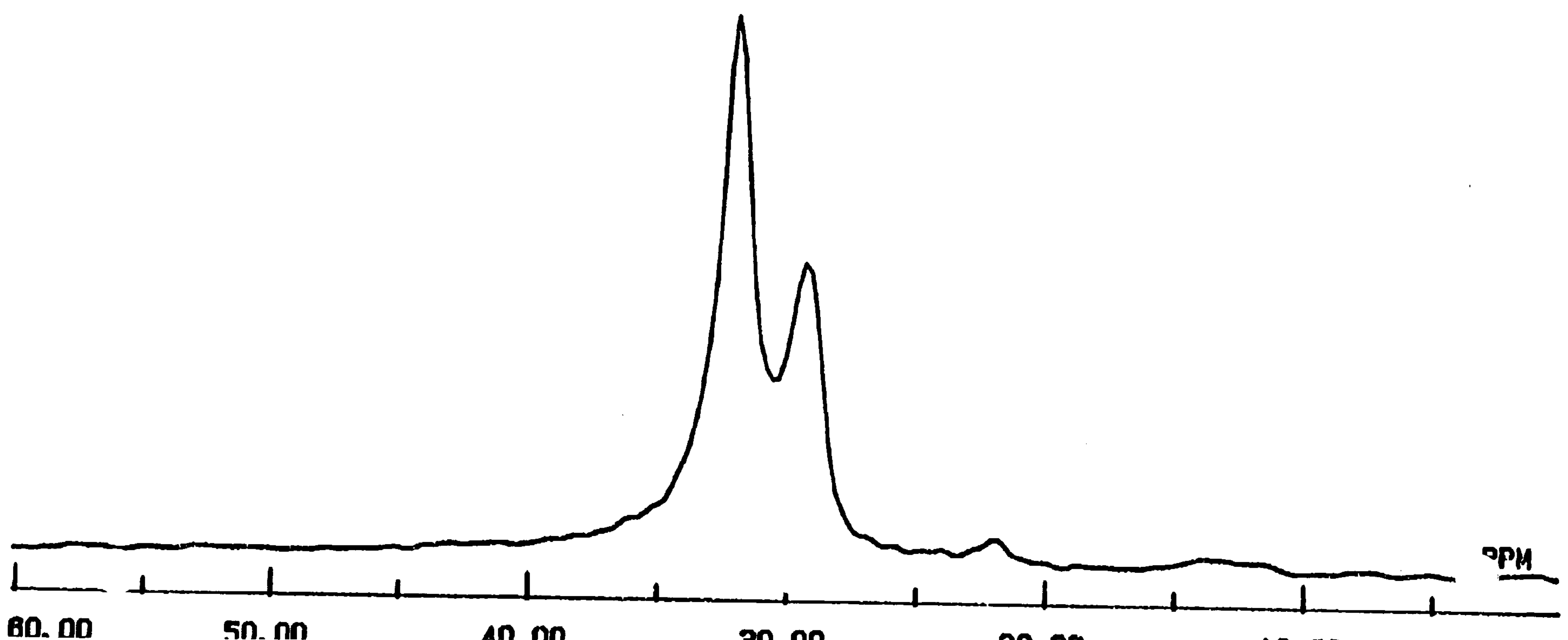


Figure 5-327. CPMAS C13 Spectrum of Used Al O_3-TiO_2 - Supported Ruthenium Catalyst 4966-124 After Soxhlet Extraction with Cyclohexane Followed by Toluene

NUC: C
NA: 24000
FOBS: 25.299380
FDEC: 100.575000
TLB: 39.028
SW: 409.82 PPM
AL: 1024
DL: 4090
PW1: 0.5 us
CT: 8.00 ms
PD: 2.00 s
FNA: HA700.A09

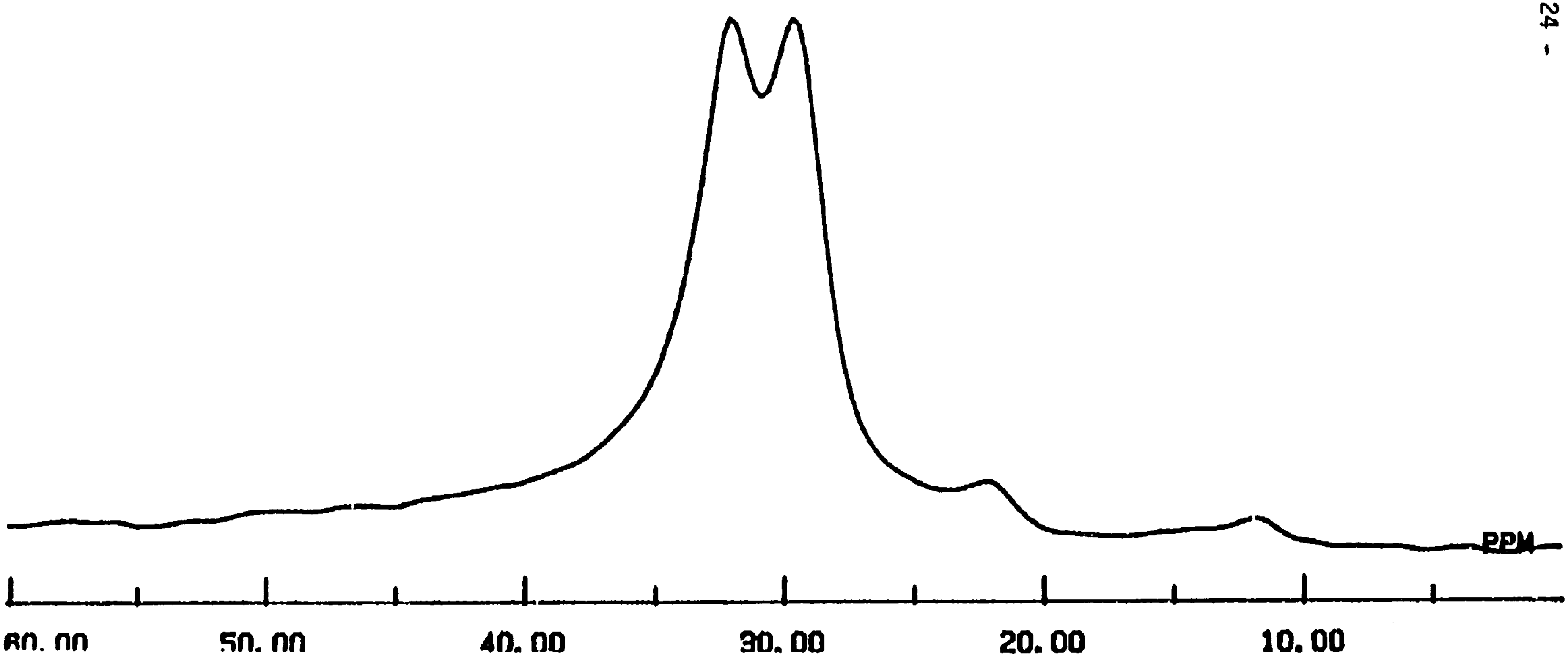
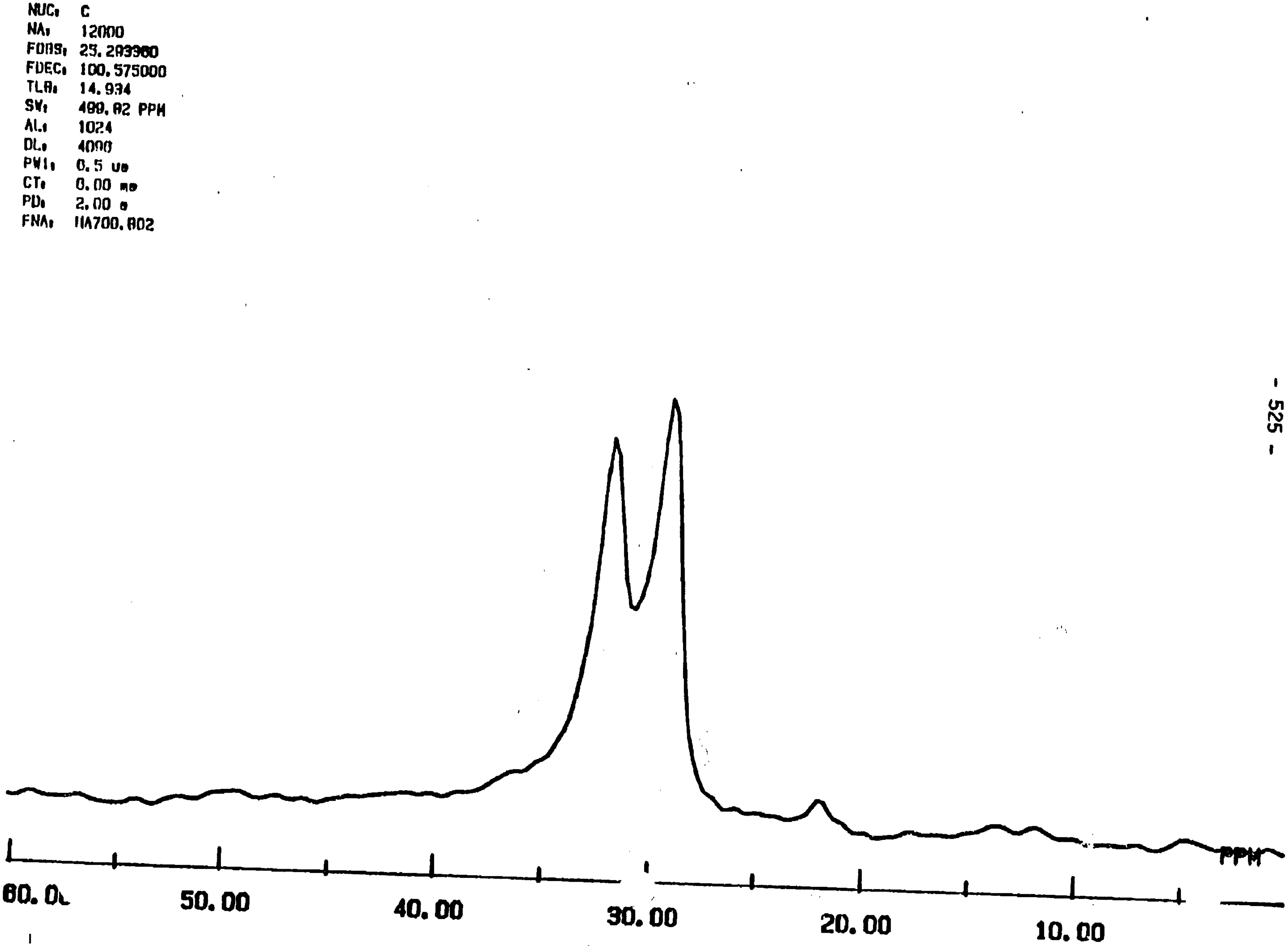
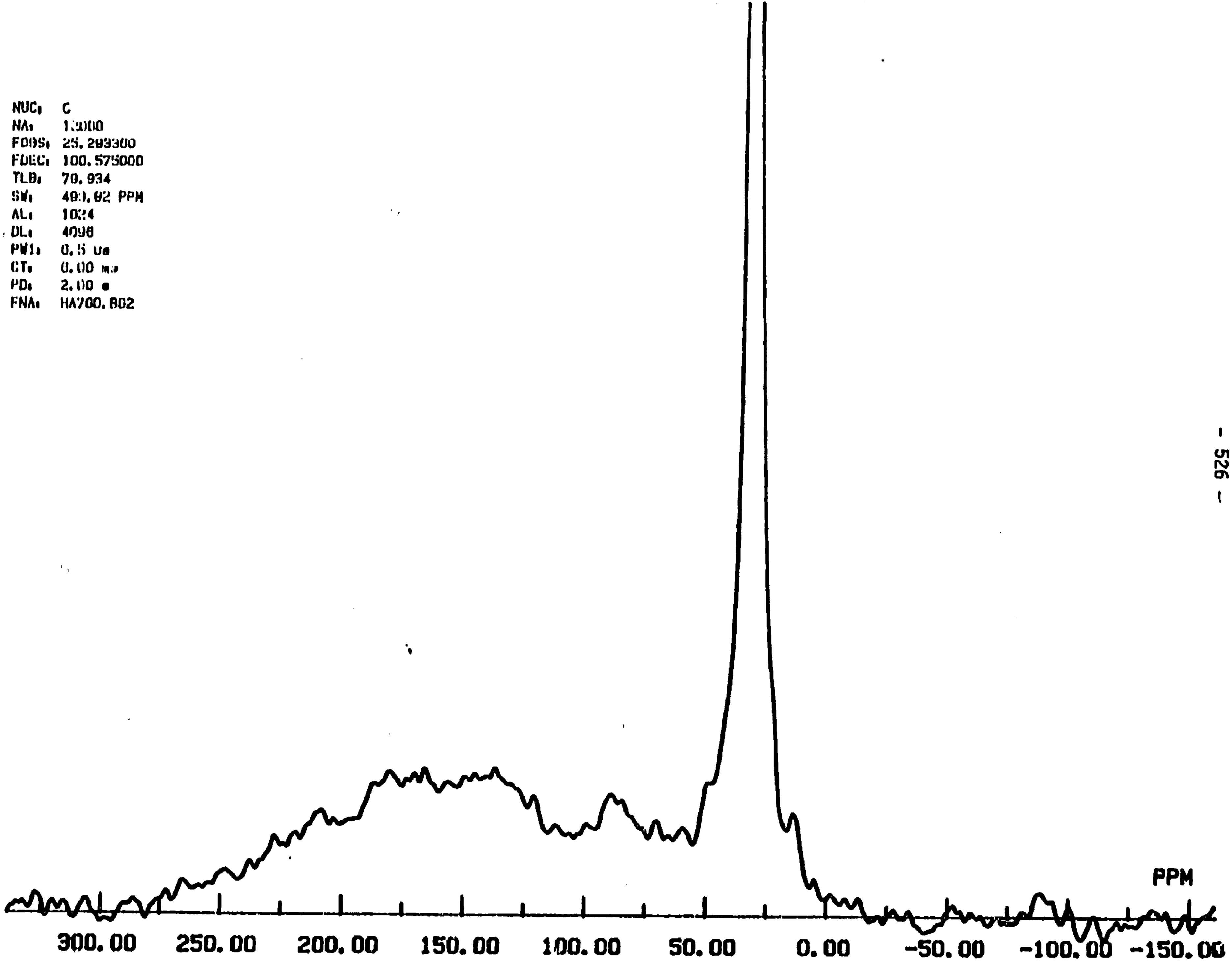


Figure 5-328. CPMAS C 13 Spectrum of Used Al_2O_3-TiO_2 - Supported Ruthenium Catalyst 4966-124 After Soxhlet Extraction with Cyclohexane Followed by Toluene and Followed by Methylene Chloride/Methanol



NUC: C
NA: 12000
FOBS: 25.203980
FDEC: 100.575000
TLB: 14.934
SW: 499.82 PPM
AL: 1024
DL: 4090
PW1: 0.5 us
CT: 0.00 ms
PD: 2.00 s
FNA: HA700.802

Figure 5-329. CPMAS C13 NMR Spectrum of Fully Extracted Used Catalyst 4966-124



```
NUC,   C
NA,    12000
FOBS,  25.289300
FDEC,  100.575000
TLB,   70.934
SW,    400.02 PPM
AL,    1024
DL,    4098
PW1,   0.5 us
CT,    0.00 ms
PD,    2.00 s
FNA,   HA700.802
```

Figure 5-330. CPMAS C13 NMR Spectrum of Fully Extracted Used Modified Ruthenium Catalyst
4966-180

```
NUC:  13C
NA:   40000
FOBS: 25.209960
FDEC: 100.581090
TLB:  19.001
SW:   592.75 PPM
AL:   1024
DL:   4000
PW1:  5.0 us
CT:   2.00 ms
PD:   2.00 s
FNA:  FTWAX.A02
```

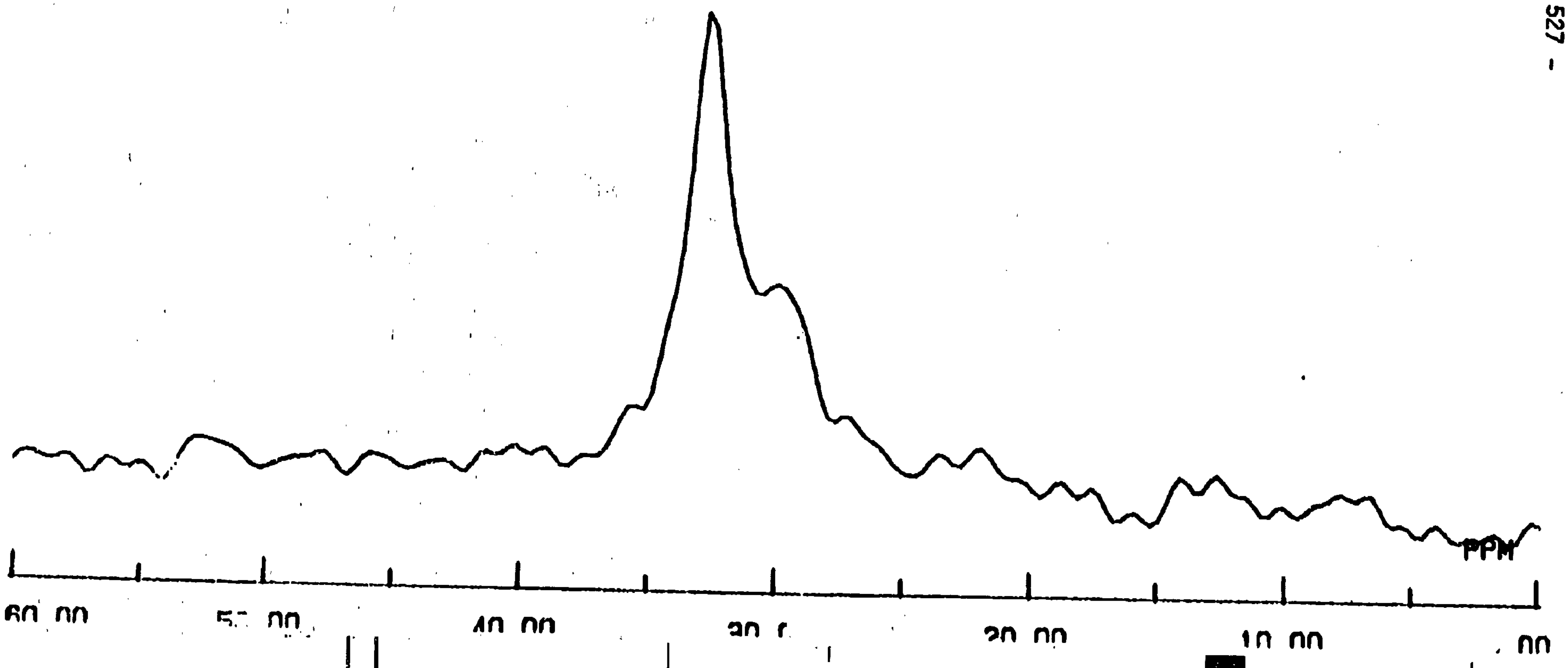
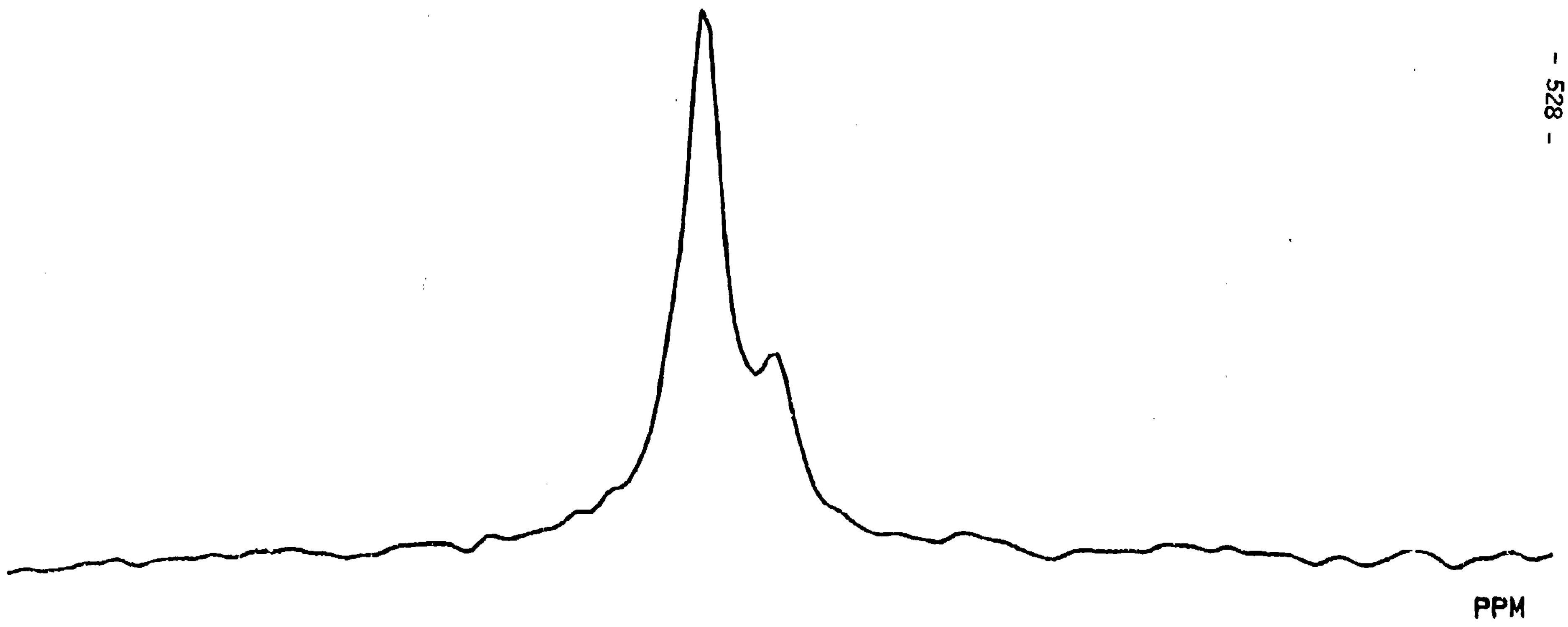


Figure 5-331. CPMAS C13 NMR Spectrum of Fully Extracted Used Unmodified Ruthenium Catalyst
4966-198

```
NUC:   13C
NA:    20000
FOBS:  25.289980
FDEC:  100.581000
TLB:   19.881
SW:    502.75 PPM
AL:    1024
DL:    4096
PW1:   5.0 us
CT:    2.00 ms
PD:    2.00 s
FNA:   FTMAX.A08
```



resonances corresponding to the immobile species in the spectra of Catalyst 4966-124 tested in Run 39. These results again indicate that the immobile carbon species have on the average much more than 44 carbons.

5.3.5.2.3.3 Overview of NMR Measurements

NMR could not detect the carbon associated with oxygen, as deteced by XPS measurements. This may indicate that the carbon associated with oxygen is present in much higher concentration at the exterior surface of the catalyst particles as detected by XPS relative to the bulk concentration measured by NMR.

NMR detected two hydrocarbon-type carbons with different mobilities, while XPS was not able to resolve two carbon species which were not associated with oxygen. Two points need to be addressed concerning the cause of the 2 ppm NMR shift between the two carbon species:

1. The mobile species can be a small portion of Fischer-Tropsch wax retained in the used catalyst despite the soxhlet extraction steps. This carbon is not expected to be chemically bound to the surface and is expected to show an NMR peak at a lower ppm relative to carbon chemically bound to the catalyst surface.

   Also, NMR shifts may possibly occur depending upon whether the wax-type hydrocarbon is inside or outside the pores of the catalyst. Finally, these differences can be explained by variations in the crystallinity of the wax.

2. The mobile and immobile carbon species probably are not part of the same β-type carbon reported by Duncan and Bell.

5.3.5.2.4 Analysis of Materials Extracted from Used Catalysts

5.3.5.2.4.1 Establishment of Experimental Procedures with Catalyst 4966-124 Tested in Run 39

Two different samples of Al_2O_3-TiO_2 supported Catalyst 4966-124 tested in Run 39 (from inlet of the reactor and from outlet of reactor) were Soxhlet extracted with cyclohexane for 7 days, followed by 4 days with toluene, and finally for 4 days with a mixture of methylene chloride and methanol.

Extraction with cyclohexane removed 56% of material from the used catalyst from the reactor inlet section as wax, while the amount of wax removed from the reactor outlet section was 40%. After extraction with cyclohexane, the inlet section had 7.91% carbon, while the outlet section had 11.76% carbon according to Leco carbon analysis (Table 5-56).

Table 5-56

Leco Carbon Analysis on Used Al_2O_3-TiO_3 Supported Ruthenium Catalyst 4966-124 After Various Soxhlet Extraction Steps

	% Sample Extracted	% C After Extraction
Cyclohexane	56% (inlet) 49% (outlet)	7.91 (inlet) 11.76 (outlet)
Toluene	2-3%	6.05 (inlet) 8.90 (outlet)
Methylene Chloride/Methanol	<1%	5.90 (inlet) 8.85 (outlet)

Further extraction with toluene only resulted in 2-3% material removal from the used catalyst. Leco carbon indicated lower carbon levels after toluene extraction on the inlet and outlet portions: 6.05% and 8.90%, respectively.

Final extraction with methylene chloride/methanol resulted in much less than 1% further material removal. The Leco carbon values for the fully extracted samples were 5.90% and 8.85%.

The extracts obtained with toluene and methylene chloride/methanol were analyzed by High Resolution Mass Spectroscopy.

The extracts obtained with toluene did not contain, in any noticeable amount, compounds other than saturated hydrocarbons which make up the Fischer-Tropsch wax.

The extracts obtained with methylene chloride/methanol, contained various compounds in addition to saturated hydrocarbons. These products are summarized in Table 5-57.

Table 5-57

HRMS Analysis of Extracts Obtained with Methylene Chloride/Methanol from the Used Catalyst 4966-124

Detected Compounds	Amount %	Carbon Number Range Detected
Saturated Hydrocarbons C_NH_{2N+2}	50-80% (inlet) 20-60% (outlet)	
Oxygenated Hydrocarbons $C_NH_{2N}O_2$ (acids and/or esters, most likely)	15-45% (inlet) 35-75% (outlet)	$\leq C_{35}$
Aromatic Hydrocarbons C_NH_{2N-Z} Z=6,8,12,14	<5%	C_{12}-C_{23}
Aromatic Oxygenates $C_NH_{2N-Z}O$ Z=6,8	<5%	C_6-C_{11}
Aromatic Dioxygenates $CnH_{2N-Z}O_2$ Z=6,8	<5%	

The majority of the compounds which were detected were saturated and oxygenated hydrocarbons. The oxygenates consisted mainly of $C_NH_{2N}O_2$ compound types. These types may be olefinic dialcohols, paraffinic acids, cyclic dialcohols, esters, ethers, keto ethers, etc. However, based on the relatively strong fragmentation peak at m/z = 60.0211, we think, these are mainly acids and/or esters.

The extracts obtained with methylene chloride/methanol were also analyzed by infrared spectroscopy (Figures 5-332 and 5-333). The spectra showed carbonyl functionality at 1710 cm^{-1} and 1745 cm^{-1}, and hydroxyl groups at 3450 cm^{-1}. These absorbances could be due to esters, acids, ketones, etc. The sample from the outlet of the catalyst showed higher absorbance at 1745 cm^{-1} and at 1168 cm^{-1}.

The minor material recovered during methylene chloride/methanol extraction was aromatic hydrocarbons and aromatic oxygenates and amounted to less than 5% of the total amount of products that were recovered. The aromatic products in two different portions of used Catalyst 4966-124 are summarized in Tables 5-58 through 5-61. Aromatic hydrocarbon types were identified as having the general formulae of C_NH_{2N-Z} (Z = 6, 8, 12 and 14). The carbon number range was C_{12}-C_{23}. Aromatic oxygenates included the following compound types: $C_NH_{2N-6}O$, $C_NH_{2N-8}O$, $C_NH_{2N-6}O_2$ and $C_NH_{2N-8}O_2$. For aromatic oxygenates the carbon number range was C_6-C_{11}.

The alkylbenzenes that were detected are plotted in Figure 5-334 in an Anderson-Schulz-Flory-type diagram. The concentration of the alkyl benzenes increased with carbon number from 14 through 17. At carbon number 18 the amount of alkylbenzene decreased substantially. The concentration increased at carbon numbers 19 and 20. The next low data point was at carbon number of 22.

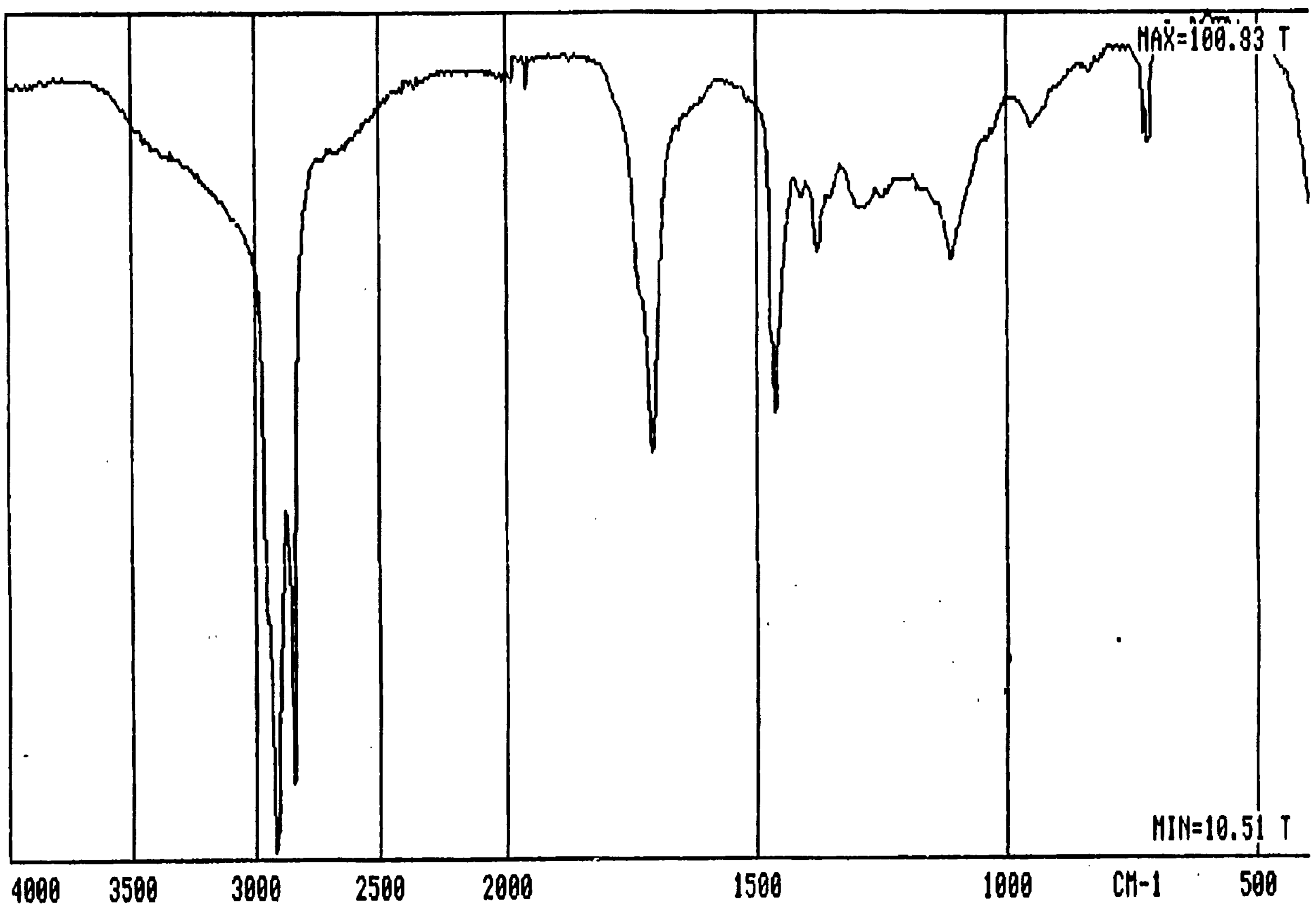


Figure 5-332: IR Spectrum of Extract Obtained with Methylene Chloride/Methanol from the Used Catalyst 4966-124 (Inlet Sample)

Figure 5-333: IR Spectrum of Extract Obtained with Methylene Chloride/Methanol from the Used Catalyst 4966-124 (Outlet Sample)

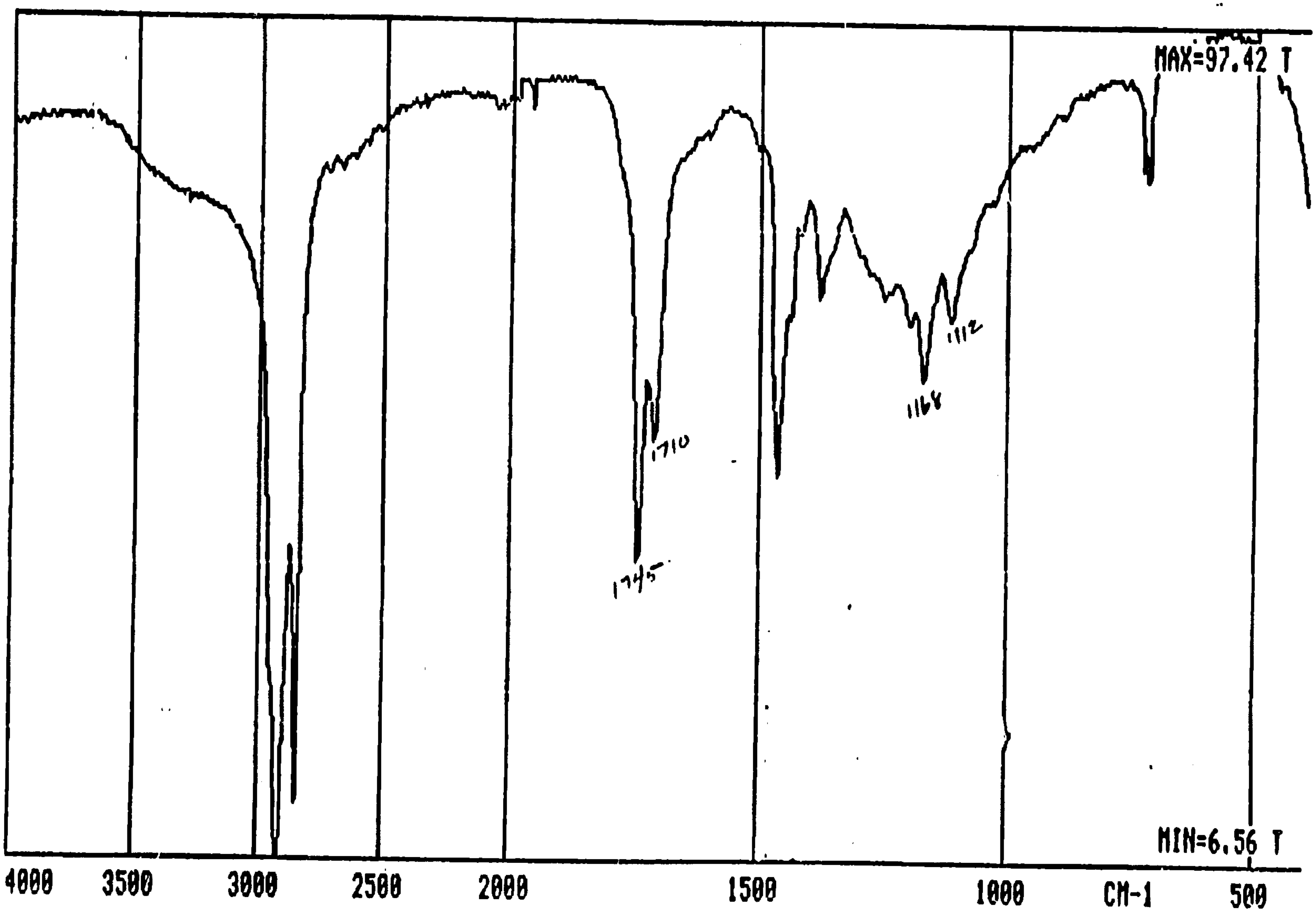


Table 5-58: Aromatic Hydrocarbons from Methylene Chloride/Methanol Extraction of Inlet Portion of Used Catalyst 4966-124

CARBON NUMBER DISTRIBUTION, WT PCT
NORMALIZED TO 100.00

AROMATIC HYDROCARBON CNH2N-Z

C NO	Z=6	Z=8	Z=10	Z=12	Z=14	Z=16	Z=18	Z=20	Z=22	Z=24	Z=26	Z=28	Z=30	Z=32	Z=34	Z=36	Z=38	Z=40
C 6	0.																	
C 7	0.																	
C 8	0.	0.																
C 9	0.	0.	0.															
C 10	0.	0.	0.	0.														
C 11	0.	0.	0.	0.														
C 12	0.	0.	0.	0.	0.	0.												
C 13	0.	0.	0.	0.	0.14	0.17												
C 14	0.89	0.30	0.	0.42	0.29	0.46	0.32											
C 15	2.16	1.22	0.	0.65	0.86	0.45	0.21	0.										
C 16	2.29	1.40	0.	0.58	0.62	0.46	0.	0.	0.									
C 17	3.45	6.08	0.	0.75	0.	0.	0.	0.	0.									
C 18	1.61	2.79	0.	1.02	0.	0.	0.	0.	0.	0.	0.							
C 19	2.54	5.16	0.	0.94	0.	0.	0.	0.	0.	0.	0.							
C 20	4.63	15.01	0.	1.83	0.	0.	0.	0.	0.	0.	0.	0.	0.					
C 21	1.60	2.25	0.	0.84	0.	0.	0.	0.	0.	0.	0.	0.	0.					
C 22	1.14	2.13	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.				
C 23	1.29	0.	0.	0.59	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.				
C 24	1.43	1.41	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.		
C 25	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.		
C 26	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 27	0.	0.	0.	2.42	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 28	0.	0.	0.	0.	2.29	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 29	0.	0.	0.	2.67	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 30	0.	0.	0.	6.72	1.78	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 31	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 32	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 33	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 34	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 35	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 36	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 37	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 38	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 39	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 40	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
TOTAL	23.03	37.75	0.	19.43	5.98	1.54	0.53	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
AVG C NO	18.79	19.20	0.00	25.02	24.45	14.78	14.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 5-59: Aromatic Compounds from Outlet Portion of Used Catalyst 4966-124

Z NO.	AROMATIC HYDROCARBON COMPOUND TYPES, CNH2N-Z •	SAMPLE WT PCT	AVG MOL WT
Z-6	BENZENES	23.88	249.03
Z-8	INDANS/TETRALINS	35.21	258.18
Z-10	DINAPHTHENE BENZENES	0.	0.00
Z-12	NAPHTHALENES	8.71	310.65
Z-14	ACENAPHTHENES/BIPHENYLS	5.36	267.80
Z-16	FLUORENES	1.50	179.16
Z-18	PHENANTHRENES/ANTHRACENES	1.30	179.70
Z-20	ACEANTHRENES	0.	0.00
Z-22	PYRENES	1.14	230.11
Z-24	CHRYSENES	0.	0.00
Z-26	CHOLANTHRENES	0.	0.00
Z-28	BENZOPYRENES	0.	0.00
Z-30	DIBENZANTHRACENES	0.	0.00
Z-32	BENZOPERYLENES	0.	0.00
Z-34	DIBENZOPYRENES	0.	0.00
Z-36	CORONENES	0.	0.00
Z-38	NAPHTHOCORONENES	0.	0.00
Z-40	DIBENZOPERYLENES	0.	0.00
Z-42	BENZOCORONENES	0.	0.00
Z-44	DINAPHTHOPYRENES	0.	0.00
Z-46	NAPHTHOCORONENES	0.	0.00
Z-48	DIBENZOCORONENES	0.	0.00
Z-50	OVALENES	0.	0.00
Z-52	PHENANTHROCORONENES	0.	0.00
Z-54	TRIBENZOCORONENES	0.	0.00
Z-56	BENZOOVALENE/PYRENOCORONENES	0.	0.00
Z-58	DIACEOVALENE	0.	0.00
Z-60	DIBENZOVALENE	0.	0.00
Z-62	TRIACEOVALYNE	0	0.00
Z-64	ACEDIBENZOOVALYNE	0.	0.00
Z-66	BENZONAPHTHOOVALENES	0.	0.00
Z-68	••• (HYDROCARBON, Z-68)	0.	0.00
Z-70	••• (HYDROCARBON, Z-70)	0.	0.00
Z-72	••• (HYDROCARBON, Z-72)	0.	0.00
Z-74	••• (HYDROCARBON, Z-74)	0.	0.00
Z-76	••• (HYDROCARBON Z-76)	0	0.00
TOTAL		77.10	258.67

Z NO.	AROMATIC OXYGENS COMPOUND TYPES, CNH2N-ZO •	SAMPLE WT PCT	AVG MOL WT
Z-60	PHENOLS	7.91	130.88
Z-80	NAPHTHENOPHENOLS	2.24	126.69
Z-100	BENZOFURANS	0.	0.00
Z-120	NAPHTHOLS	0.	0.00
Z-140	NAPHTHENONAPHTHOLS	0.	0.00
Z-160	DIBENZOFURANS	0.	0.00
Z-180	HYDROXYANTHRACENES	0.	0.00
Z-200	HYDROXYNAPHTHENOANTHRACENES	0.	0.00
Z-220	HYDROXYPYRENES	0.	0.00
Z-240	HYDROXYCHRYSENES	0.	0.00
Z-260	HYDROXYCHOLANTHRENES	0.	0.00
Z-280	HYDROXYBENZOPYRENES	0.	0.00
Z-300	HYDROXYDIBENZANTHRACENES	0.	0.00
Z-320	HYDROXYBENZOPERYLENES	0.	0.00
Z-340	HYDROXYBENZOPYRENES	0.	0.00
Z-360	HYDROXYCORONENES	0	0.00
Z-380	HYDROXYNAPHTHOCORONENES	0.	0.00
Z-400	HYDROXYDIBENZOPERYLENES	0.	0.00
Z-420	HYDROXYBENZOCORONENES	0.	0.00
Z-440	HYDROXYDINAPHTHOPYRENES	0.	0.00
Z-460	HYDROXYNAPHTHOCORONENES	0.	0.00
Z-480	HYDROXYDIBENZOCORONENES	0.	0.00
Z-500	HYDROXYOVALENES	0.	0.00
Z-520	HYDROXYPHENANTHROCORONENES	0.	0.00
Z-540	HYDROXYTRIBENZOCORONENES	0.	0.00
Z-560	HYDROXYBENZOOVALENE	0.	0.00
Z-580	HYDROXYDIACEOVALENE	0.	0.00
Z-600	HYDROXYDIBENZOVALENE	0.	0.00
TOTAL		10.15	129.95

Z NO.	AROMATIC 2-OXYGENS COMPOUND TYPES, CNH2N-ZO2 •	SAMPLE WT PCT	AVG MOL WT
Z-402	• (2-OXYGEN, Z-402)	9.80	126.15
Z-602	• (2-OXYGEN, Z-602)	1.07	118.55
Z-802	• (2-OXYGEN, Z-802)	1.88	152.16
Z-1002	• (2-OXYGEN, Z-1002)	0.	0.00
Z-1202	• (2-OXYGEN, Z-1202)	0.	0.00
Z-1402	• (2-OXYGEN, Z-1402)	0.	0.00
Z-1602	• (2-OXYGEN, Z-1602)	0.	0.00
Z-1802	• (2-OXYGEN, Z-1802)	0.	0.00
Z-2002	• (2-OXYGEN, Z-2002)	0.	0.00
Z-2202	• (2-OXYGEN, Z-2202)	0.	0.00
Z-2402	• (2-OXYGEN, Z-2402)	0.	0.00
Z-2602	• (2-OXYGEN, Z-2602)	0.	0.00
Z-2802	• (2-OXYGEN, Z-2802)	0.	0.00
Z-3002	• (2-OXYGEN, Z-3002)	0.	0.00
Z-3202	• (2-OXYGEN, Z-3202)	0.	0.00
Z-3402	• (2-OXYGEN, Z-3402)	0.	0.00
Z-3602	• (2-OXYGEN, Z-3602)	0.	0.00
Z-3802	• (2-OXYGEN, Z-3802)	0.	0.00
Z-4002	• (2-OXYGEN, Z-4002)	0.	0.00
Z-4202	• (2-OXYGEN, Z-4202)	0.	0.00
Z-4402	• (2-OXYGEN, Z-4402)	0.	0.00
Z-4602	• (2-OXYGEN, Z-4602)	0.	0.00
Z-4802	• (2-OXYGEN, Z-4802)	0.	0.00
Z-5002	• (2-OXYGEN, Z-5002)	0.	0.00
Z-5202	• (2-OXYGEN, Z-5202)	0.	0.00
Z-5402	• (2-OXYGEN, Z-5402)	0.	0.00
Z-5602	• (2-OXYGEN, Z-5602)	0.	0.00
Z-5802	• (2-OXYGEN, Z-5802)	0.	0.00
Z-6002	• (2-OXYGEN, Z-6002)	0	0.00
TOTAL		12.75	129.35

Table 5-60: Aromatic Hydrocarbons from Methylene Chloride/Methanol Extraction of Outlet Portion of Used Catalyst 4966-124

CARBON NUMBER DISTRIBUTION, WT PCT
NORMALIZED TO 100.00

AROMATIC HYDROCARBON CNH2N-Z

C NO	Z=6	Z=8	Z=10	Z=12	Z=14	Z=16	Z=18	Z=20	Z=22	Z=24	Z=26	Z=28	Z=30	Z=32	Z=34	Z=36	Z=38	Z=40
C 6	0.																	
C 7	0.																	
C 8	0.	0.																
C 9	0.	0.	0.															
C 10	0.	0.	0.	0.														
C 11	0.	0.	0.	0.														
C 12	0.	0.	0.	0.	0.	0.												
C 13	0.	0.	0.	0.93	0.45	0.66												
C 14	0.88	0.	0.	1.18	0.36	0.56	1.15											
C 15	2.86	0.	0.	1.06	1.44	0.	0.15	0.										
C 16	3.17	2.08	0.	0.	0.98	0.28	0.	0.	0.									
C 17	4.26	6.01	0.	0.78	0.	0.	0.	0.	0.									
C 18	1.93	2.79	0.	0.	0.	0.	0.	0.	1.14	0.	0.							
C 19	2.89	6.39	0.	0.	0.	0.	0.	0.	0.	0.	0.							
C 20	4.96	14.97	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.					
C 21	0.	2.97	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.					
C 22	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.				
C 23	2.93	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.				
C 24	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.		
C 25	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.		
C 26	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 27	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 28	0.	0.	0.	0.	2.13	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 29	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 30	0.	0.	0.	4.76	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 31	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 32	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 33	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 34	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 35	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 36	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 37	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 38	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C 39	0.	0	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0	0
C 40	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
TOTAL	23.88	35.21	0.	8.71	5.36	1.50	1.30	0.	1.14	0	0.	0.	0.	0.	0.	0.	0.	0.
AVG C NO	18.20	19.00	0.00	23.03	20.11	13.93	14.12	0.00	18.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 5-61: Aromatic Compounds from Inlet Portion of Used Catalyst 4966-124

Z NO.	AROMATIC HYDROCARBON COMPOUND TYPES. CNH2N-Z •	SAMPLE WT PCT	AVG MOL WT
Z-6	BENZENES	23.03	257.26
Z-8	INDANS/TETRALINS	37.75	260.99
Z-10	DINAPHTHENE BENZENES	0.	0.00
Z-12	NAPHTHALENES	19.43	338.52
Z-14	ACENAPHTHENES/BIPHENYLS	5.98	328.59
Z-16	FLUORENES	1.54	191.02
Z-18	PHENANTHRENES/ANTHRACENES	0.53	183.63
Z-20	ACEANTHRENES	0.	0.00
Z-22	PYRENES	0.	0.00
Z-24	CHRYSENES	0.	0.00
Z-26	CHOLANTHRENES	0.	0.00
Z-28	BENZOPYRENES	0.	0.00
Z-30	DIBENZANTHRACENES	0.	0.00
Z-32	BENZOPERYLENES	0.	0.00
Z-34	DIBENZOPYRENES	0.	0.00
Z-36	CORONENES	0	0.00
Z-38	NAPHTHOCORONENES	0.	0.00
Z-40	DIBENZOPERYLENES	0.	0.00
Z-42	BENZOCORONENES	0.	0.00
Z-44	DINAPHTHOPYRENES	0.	0.00
Z-46	NAPHTHOCORONENES	0.	0.00
Z-48	DIBENZOCORONENES	0.	0.00
Z-50	OVALENES	0.	0.00
Z-52	PHENANTHROCORONENES	0.	0.00
Z-54	TRIBENZOCORONENES	0.	0.00
Z-56	BENZOOVALENE/PYRENOCORONENES	0.	0.00
Z-58	DIACEOVALENE	0.	0.00
Z-60	DIBENZOVALENE	0.	0.00
Z-62	TRIACEOVALYNE	0.	0.00
Z-64	ACEDIBENZOOVALYNE	0.	0.00
Z-66	BENZONAPHTHOOVALENES	0.	0.00
Z-68	••• (HYDROCARBON, Z-68)	0	0.00
Z-70	••• (HYDROCARBON, Z-70)	0.	0.00
Z-72	••• (HYDROCARBON, Z-72)	0.	0.00
Z-74	••• (HYDROCARBON, Z-74)	0.	0.00
Z-76	••• (HYDROCARBON, Z-76)	0	0.00
TOTAL		89.26	279.98

Z NO.	AROMATIC OXYGENS COMPOUND TYPES. CNH2N-ZO •	SAMPLE WT PCT	AVG MOL WT
Z-60	PHENOLS	4.28	126.82
Z-80	NAPHTHENOPHENOLS	1.97	155.06
Z-100	BENZOFURANS	0.52	142.57
Z-120	NAPHTHOLS	0.	0.00
Z-140	NAPHTHENONAPHTHOLS	0.	0.00
Z-160	DIBENZOFURANS	0.	0.00
Z-160	HYDROXYANTHRACENES	0.	0.00
Z-200	HYDROXYNAPHTHENOANTHRACENES	0.	0.00
Z-220	HYDROXYPYRENES	0.	0.00
Z-240	HYDROXYCHRYSENES	0.	0.00
Z-260	HYDROXYCHOLANTHRENES	0.	0.00
Z-280	HYDROXYBENZOPYRENES	0.	0.00
Z-300	HYDROXYDIBENZANTHRACENES	0.	0.00
Z-320	HYDROXYBENZOPERYLENES	0.	0.00
Z-340	HYDROXYBENZOPYRENES	0.	0.00
Z-360	HYDROXYCORONENES	0.	0.00
Z-380	HYDROXYNAPHTHOCORONENES	0.	0.00
Z-400	HYDROXYDIBENZOPERYLENES	0.	0.00
Z-420	HYDROXYBENZOCORONENES	0.	0.00
Z-440	HYDROXYDINAPHTHOPYRENES	0.	0.00
Z-460	HYDROXYNAPHTHOCORONENES	0.	0.00
Z-480	HYDROXYDIBENZOCORONENES	0.	0.00
Z-500	HYDROXYOVALENES	0.	0.00
Z-520	HYDROXYPHENANTHROCORONENES	0.	0.00
Z-540	HYDROXYTRIBENZOCORONENES	0.	0.00
Z-560	HYDROXYBENZOOVALENE	0.	0.00
Z-580	HYDROXYDIACEOVALENE	0.	0.00
Z-600	HYDROXYDIBENZOVALENE	0.	0.00
TOTAL		6.77	130.25

Z NO.	AROMATIC 2-OXYGENS COMPOUND TYPES. CNH2N-ZO2 •	SAMPLE WT PCT	AVG MOL WT
Z-402	• (2-OXYGEN, Z-402)	2.97	133.57
Z-602	• (2-OXYGEN, Z-602)	0.35	138.07
Z-802	• (2-OXYGEN, Z-802)	1.64	151.78
Z-1002	• (2-OXYGEN, Z-1002)	0.	0.00
Z-1202	• (2-OXYGEN, Z-1202)	0.	0.00
Z-1402	• (2-OXYGEN, Z-1402)	0	0.00
Z-1602	• (2-OXYGEN, Z-1602)	0.	0.00
Z-1802	• (2-OXYGEN, Z-1802)	0.	0.00
Z-2002	• (2-OXYGEN, Z-2002)	0.	0.00
Z-2202	• (2-OXYGEN, Z-2202)	0.	0.00
Z-2402	• (2-OXYGEN, Z-2402)	0.	0.00
Z-2602	• (2-OXYGEN, Z-2602)	0.	0.00
Z-2802	• (2-OXYGEN, Z-2802)	0.	0.00
Z-3002	• (2-OXYGEN, Z-3002)	0.	0.00
Z-3202	• (2-OXYGEN, Z-3202)	0.	0.00
Z-3402	• (2-OXYGEN, Z-3402)	0.	0.00
Z-3602	• (2-OXYGEN, Z-3602)	0.	0.00
Z-3802	• (2-OXYGEN, Z-3802)	0.	0.00
Z-4002	• (2-OXYGEN, Z-4002)	0.	0.00
Z-4202	• (2-OXYGEN, Z-4202)	0.	0.00
Z-4402	• (2-OXYGEN, Z-4402)	0.	0.00
Z-4602	• (2-OXYGEN, Z-4602)	0.	0.00
Z-4802	• (2-OXYGEN, Z-4802)	0.	0.00
Z-5002	• (2-OXYGEN, Z-5002)	0.	0.00
Z-5202	• (2-OXYGEN, Z-5202)	0.	0.00
Z-5402	• (2-OXYGEN, Z-5402)	0	0.00
Z-5602	• (2-OXYGEN, Z-5602)	0.	0.00
Z-5802	• (2-OXYGEN, Z-5802)	0.	0.00
Z-6002	• (2-OXYGEN, Z-6002)	0.	0.00
TOTAL		4.97	139.90

• SUGGESTED COMPOUND TYPES

Figure 5-334. Anderson-Schulz-Flory-Type Distribution for Alkyl Benzenes from Inlet Portion of Used Catalyst 4966-124