

CHARACTERIZATION OF PETROLEUM RESID COMPONENTS FRACTIONATED BY HIGH VACUUM SHORT-PATH DISTILLATION AND GEL PERMEATION CHROMATOGRAPHY

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INTRODUCTION

The traditional cut point between distillable oils and resids by vacuum distillation is 1000°C. The recent advent of high vacuum, short-path distillation (DISTACT molecular still) makes it possible to cut deeper into resid components (see references cited in ref 1). By varying the wall temperature and pressure of the DISTACT unit, the 1000+°F resid components can be further cut into narrow boiling fractions up to an atmospheric equivalent end point of about 1350°F. In this study, this additional resid components distillable between 1000 and 1350°F was fractionated and characterized. Furthermore, the asphaltenes in the bottom material were separated into molecular weight cuts by GPC (Gel permeation Chromatography). Such fractionation scheme allows us to compare systematically the composition and properties of the full range petroleum resid components as a function of AEBP (Atmospheric Equivalent Boiling Point) or molecular weight.

EXPERIMENTAL

The two feedstocks used in this study were both high sulfur 1000+°F petroleum vacuum resids originated from different crude blends. The two are similar in general properties as shown in Table 1. The DISTACT fractionation scheme is illustrated in Figure 1, which lists the different temperature and pressure combinations used to cut the different boiling fractions. The AEBPs of the fractions were measured by GC simulated distillation. The GPC separation was carried out on a Waters GPC system using a set of Water Styragel columns arranging in the order of 60, 100, 100 and 500 Å pore sizes. The dimensions of each of the columns were 7 mm i.d. and 100 cm long. The elution solvent was tetrahydrofuran and the flow rate was 5 ml/min. Multiple runs were made in order to collect sufficient material for characterization. The VPO (Vapor Pressure Osmometry) measurement were made in nitrobenzene solvent at 120°C, using infinite dilution method.

Three LC (Liquid Chromatographic) procedures were used for compound type separation. The IX (Ion Exchange) separation used two sequentially connected columns each packed with anion (MP 1 resin for trapping acids) or cation (MP 50 resin for trapping bases) exchange resins obtained from Biorad. The neutrals were eluted by toluene from the column sequence while the acidic and basic material were desorbed from their respective columns by isopropanol/toluene solvent mixed with minor amounts of formic acids or isopropylamine, respectively. The ABN (Acid/Base/Neutral) separation by alumina LC was carried out on two sequentially connected columns packed with acidic (for trapping bases) and basic (for trapping acids and pyrrolics) alumina, respectively. The neutrals were eluted from the column sequence by cyclohexane (neutral I) and toluene (Neutral II). Afterwards, the two columns were disconnected and the pyrrolics in the basic alumina column was first eluted by dichloromethane. Finally, a mixture of dichloromethane and methanol was used to elute the acids and bases from their respective columns. In ORA separation, the asphaltenes and maltenes were first separated by hexane dissolution. The maltenes were then separated by Silica Gel LC into oil and resin fractions.

The NMR hydrocarbon analysis was based on data from combined H-1 and C-13 solution NMR analysis using the Brown-Lader model (2).

RESULTS AND DISCUSSION

1. Properties of DISTACT fractions: The boiling curves of the fractions from GC simulated distillation are shown in Figure 2. In Table 2, the wt % yield and the boiling ranges are listed. The BP data show a progressive increase in boiling range from the lighter to the heavier fractions, indicating the validity of the DISTACT distillation technique in terms of BP separation. The four distillable fractions from O3 through O6 account for 61% of the total resid material, with their T50 temperature (temperature at which 50 wt% is distillable) increases regularly from 840, 980, 1080 to 1090°F. The end points of the two bottom cuts, R1 and R2, are both above 1400°F. Their T50 points are in the 1320-1350°F range. Overall, about 80 wt% of the total 1000+°F resid mass is DISTACT distillables.

The ORA yield and elemental composition in Tables 3 and 4 indicate that as the BP of the fractions increases, the H/C ratio decreases and the concentrations of asphaltenes, Rams carbon and heteroatoms increase regularly. On a resid feed basis, the four distillate fractions account for 16% of the Rams carbon, 29% N, 43% S and 10-12% Ni/V. Thus, while the higher cut point of the DISTACT technique significant increases the distillable yield, it also allows the carryover of significant amounts of catalyst poisons.

The MW data for the DISTACT fractions are listed in Table 8 along with the NMR results to be discussed later. The number average MWs of the fractions obtained by GPC and VPO agree very well. The MW increases regularly from 400 for fraction O6 to 8-900 for O3 and 14-1500 for the bottom fraction R1, in the same direction as the BP.

**2. Compound Type Separation:** The compound type distribution of the DISTACT distillables was studied by IX and Alumina ABN separation using resid B as the sample. In both cases, a "normal" and a "reversed" column separation procedures were carried out. The yield distribution and the elemental composition of the fractions from the two separations are summarized in Tables 5 (IX) and 6 (Alumina). In IX separation, the total mass recovery is 98% in the normal sequence and only 93.7 % in the reversed one, indicating small material losses due to irreversible adsorption by IX resins, especially the cation IX resin. The mass recovery in the alumina separation is essentially quantitative irrespective of the column sequence. The yield of the total polar material (acids plus bases) in alumina separation is lower than those of IX (12-13 vs 18-20%). Furthermore, the alumina LC gives similar acid/base yield distributions after column switching whereas different results were obtained in the IX case. It is likely that the IX resins adsorb significant amounts of extra high MW polyaromatics in addition to the N/O containing polar species because of their high adsorptivities. This extra material can locate themselves in either the acid or base fractions depending on the order of the columns.

Based on the more consistent alumina ABN separation, the neutral material amounts to about 88-90% of the total distillables. The three polar fractions--pyrrolics, acids and bases--account for only 10-12% of the total mass but 98-99% of the total N and metals. The S is more evenly distributed (IX results). The low H/C ratios of the polar fractions (1.0-1.3) indicate their highly aromatic nature. The MWs of the ABN fractions differ only slightly: 570 for neutrals compared to 580-600 for acids and bases. The order is consistent with the BP curves as shown on the right of Figure 2.

The highly functionalized structure of the three polar fractions are evidenced from their FTIR spectra shown in Figure 3. The pyrrolic fraction shows a strong band around 3500  $\text{cm}^{-1}$ , indicative of N-H absorption. The acids show a series of bands from 3400-3650  $\text{cm}^{-1}$ , indicative of phenolic O-H with varying extent of H bondings. All three polar fractions distinguish themselves from the two neutral fractions by their prominent carbonyl absorption bands around 1650-1750  $\text{cm}^{-1}$ . The pyrrolics and the bases also show the aromatic C-C and C-N bands around 1550-1620  $\text{cm}^{-1}$ , suggesting the presence of N in the ring systems. On the other hand, the spectra of the two neutral fractions show only typical hydrocarbon structure free of any heteroatom functionalities.

In Table 7, the MW, % aromatic C, MW and ABN yield distribution between the gas oils and the DISTACT distillates are compared.

**3. NMR Average Structure:** The polyaromatic structure of the DISTACT fractions were determined by combined C-13 and H-1 NMR analyses using the improved Brown-Lader model (2). The model assumes that all the molecules being analyzed are aromatic with the aliphatics present only as side chains on the polyaromatic core. Thus, before NMR analysis, the aliphatics in the ABN neutrals of the DISTACT fractions were further separated by Silica Gel LC. Such separation showed that the DISTACT bottom fractions (R1 and R2) contain only 0.04-0.05 wt% of pure aliphatic components. In the distillate portion, the aliphatics in the four lighter fractions O4 through O6 is less than 5%, but as much as 41% was found in the heaviest fraction O3.

Table 8 lists the NMR-derived average molecular structural parameters for the DISTACT fractions of resid A. The  $C_c$  increases smoothly from 21.4 to 36.9% with increasing boiling range of the fractions. The cluster ring number (number of aromatic rings in the polyaromatic core) also increases with boiling range from an average of 1.6 rings for O6 to 5.4 rings for the heaviest fraction R1. The cluster weights of the average molecule in the fractions are compared with their

corresponding MWs measured by VPO and GPC. For the four distillate fractions O3 through O6, the cluster weight and the MW for each fraction is fairly close. Within the uncertainties of the average structure determinations, the data suggest that the molecules in the distillates on the average contain only one cluster. This is opposed to the residue fraction R1 where the MW is about twice that of the cluster weight. Thus, the average molecule in R1 contains about 2 clusters.

**4. Asphaltenes:** Asphaltenes represent the heaviest component in resids. As shown earlier, nearly all the asphaltenes are in the DISTACT bottom material. The asphaltenes in the DISTACT bottom of resid B was fractionated by GPC into seven MW fractions. Essentially quantitative mass recovery was observed in GPC separations.

The MW of the separated fractions were further determined by both VPO and analytical GPC. The yield distribution, elemental composition, MW and NMR derived structural parameters of the GPC fractions are summarized in Table 9. The data show that the major differences among the different fractions are MW and NMR structure parameters, while the elemental and metal concentrations are grossly similar. The MW increases smoothly from less than 620 for the lightest cut 7 to 50-5100 for the two heaviest cuts 1 and 2.

The NMR data show that about 55 wt% of the asphaltenes (sum of cuts 4 through 7) has an average cluster size of 4-6 rings. The total of cuts 2 and 3, which account for 35% of the asphaltenes, has about 6-7 rings. The heaviest asphaltenes (cut 1), which accounts for 10 wt% of the total asphaltenes and 1.2 wt% of the resid mass, has an average of 14 rings. Comparing the cluster weight with the MW of the fractions, it is seen that all but fraction 6 have multiple clusters per average molecule. The number of clusters per molecule increases with the MW of the fractions from 3-4 clusters for fractions 4 and 5 to 6-10 clusters for fractions 2 and 3. The heaviest fraction 1 has the highest number of rings per cluster (14) but only 5 clusters per average molecule.

#### SUMMARY

The composition and properties of resid components as a function of increasing BP or MW are compared in Table 10. Results show satisfactory BP separation of the maltenes by DISTACT and MW separation of the asphaltenes by GPC. A comparison among the properties of gas oils, DISTACT fractions and GPC MW cuts show that there is a continuous and smooth increase of aromaticity, polarity and NMR derived polyaromatic cluster size with BP or MW. The same compound types exist in different boiling fractions but the relative amounts of the different types change with BP. The commonly suggested "structural discontinuity" between asphaltenes and other heavy oil components is not apparent except for the heaviest asphaltene fractions, which account for about 1.2 wt% of the total resid mass. However, the analytical data for this fractions of heavy and highly polar material remain questionable because of their reactive nature.

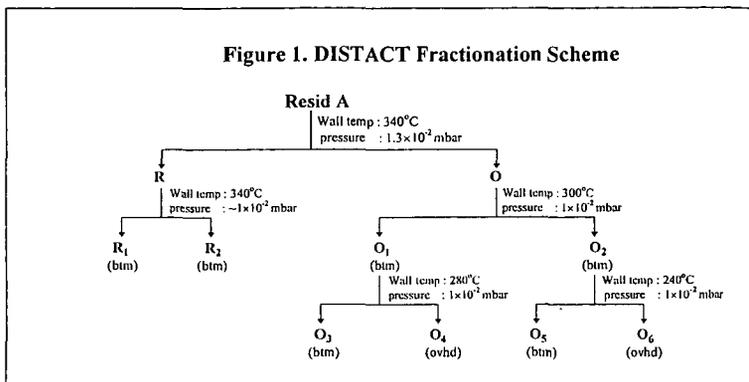
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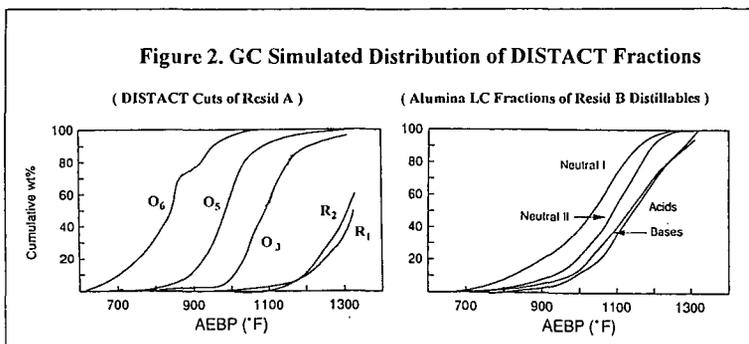
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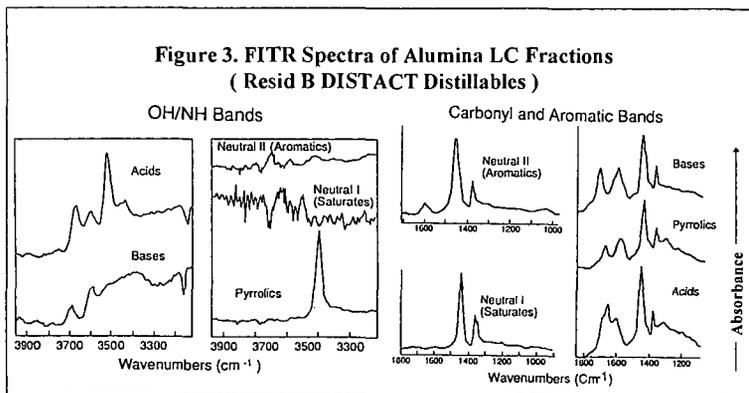
**Figure 1. DISTACT Fractionation Scheme**



**Figure 2. GC Simulated Distribution of DISTACT Fractions**



**Figure 3. FITR Spectra of Alumina LC Fractions (Resid B DISTACT Distillables)**



**TABLE 1**  
**RESID FEED PROPERTIES**

Properties	Virgin High-S Resid A	Virgin Resid B
Wt% C	84.10	84.72
Wt% H	10.29	10.35
Wt% S	4.64	3.75
Wt% N	0.51	0.52
PPM, Ni	50	56
PPM, V	228	222
H/C	1.46	1.47
% C <sub>A</sub>	30.0	32.6
Wt% Rams	17.1	20.0
Wt% 1000-°F	18	0
ORA (Wt%):		
Oil	30.0	40.9
Resin	58.2	46.2
Asphaltene	9.6	12.9

**TABLE 2**  
**DISTACT FRACTION YIELD AND BOILING RANGE BY GC SIMULATED DISTILLATION (RESID A)**

Boiling Range				
Fraction Code	Wt%	IDP	T50	T90
R <sub>1</sub>	37.4	900	1350	> 1400
R <sub>2</sub>	6.6	1000	1320	> 1400
O <sub>3</sub>	5.6	700	1080	1250
O <sub>4</sub>	23.0	700	1090	1220
O <sub>5</sub>	12.3	700	980	1090
O <sub>6</sub>	15.0	600	840	960

IDP = Initial Boiling Point; T50 and T90 = °C when 50 and 90 wt%, respectively, of materials are distillable.

**TABLE 3**      **ORA AND RAMSCARBON YIELDS OF DISTACT FRACTIONS (RESID A)**

Fraction	Oil	Resin	Asphaltenes	Total	Rams C
	Wt%				
R <sub>1</sub>	5.7	68.5	22.7	96.9	32.9
R <sub>2</sub>	7.5	69.3	21.3	98.1	33.1
O <sub>3</sub>	28.5	66.8	4.0	99.3	12.8
O <sub>4</sub>	39.6	58.9	1.2	99.7	7.4
O <sub>5</sub>	53.4	46.6	0.2	100.2	2.2
O <sub>6</sub>	65.2	34.4	0.1	99.7	0.3
Weighted Sum of Above Fractions	29.7	58.4	10.5	98.6	17.2
Feed by Direct Analysis	30.0	58.2	9.6	97.8	-

**TABLE 4**      **ELEMENTAL COMPOSITION OF DISTACT CUTS (RESID A)**

Fraction	C	H	N	O (by difference)	S	Total Metals	H/C
	Wt%						
R <sub>1</sub>	83.50	9.09	0.70	0.49	6.16	0.06	1.31
R <sub>2</sub>	83.77	9.39	0.69	0.03	6.07	0.05	1.35
O <sub>3</sub>	83.98	10.61	0.37	0.74	4.28	0.02	1.51
O <sub>4</sub>	84.54	11.07	0.27	0.22	3.89	0.01	1.57
O <sub>5</sub>	85.13	11.26	0.21	0.24	3.61	< 0.01	1.59
O <sub>6</sub>	85.28	11.69	0.12	0.05	2.86	< 0.01	1.64

**TABLE 5**  
**ELEMENTAL COMPOSITION OF COMPOUND-TYPE FRACTIONS SEPARATED BY ION-EXCHANGE LC**  
**(Resid B; DISTACT distillate)\***

	Original Sample* (Direct Measurement)	Reversed Column Sequence (Cation + Anion Resins)				Normal Column Sequence (Anion + Cation Resins) †			
		Neutrals	Acids	Bases	Calculated Sum of Fractions	Neutrals	Acids	Bases	Calculated Sum of Fractions
Wt% Yield	= 100	80.4	8.0	9.9	98.3	74.0	14.1	5.6	93.7
Wt% C	85.31	84.87	82.56	82.29	84.43	85.09	83.45	81.55	84.63
Wt% H	11.17	11.54	9.28	8.51	11.05	11.59	8.87	8.94	11.02
Wt% N	0.28	< 0.01	1.66	1.45	0.28	< 0.01	1.79	0.81	0.30
Wt% S	3.06	2.18	3.81	2.93	2.39	2.15	3.5	2.12	2.35
Wt% Total Metals	--	< 0.01	0.05	0.07	--	< 0.01	0.07	< 0.01	< 0.01
Elemental Sum: Wt%	96.8	98.8	97.3	95.3	98.2	98.9	97.1	93.4	98.3
PPM Ni	9	0.4	102	15	10	0.4	85	< 5	12
PPM V	68	0	151	153	27	0.2	430	< 2	60
H/C	1.57	1.63	1.35	1.22	1.57	1.63	1.28	1.32	1.56

\*The fraction has an ORA distribution of 65.1% oil, 34.6% resin, and 0.3% asphaltenes.

† In ion exchange separation, two columns, one packed with cation resin and the others packed with anion resins, are connected in series. The basic material is trapped on the cation resins whereas the acidic material is trapped on the anion resins. The reverse sequence has the cation column in front of the anion column, whereas the reverse is true in the normal sequence.

**TABLE 6**  
**ELEMENT COMPOSITION OF COMPOUND-TYPE FRACTIONS SEPARATED BY ALUMINA LC**  
**(Resid B; DISTACT distillate)**

Fraction	Normal LC Sequence (Basic + Acidic Alumina, Acid Material First)					Reversed LC Sequence (Acidic + Basic Alumina, Basic Materials First)				
	Yield	C	H	N	H/C	Yield	C	H	N	H/C
wt %										
(Standard As-Received Alumina, 2% H <sub>2</sub> O)										
Neutral I (Cyclohexane Elution)	35.6	86.21	13.34	(2 ppm)	1.86	56.4	85.38	12.69	(6 ppm)	1.78
Neutral II (Toluene Elution)	53.5	84.35	9.95	(128 ppm)	1.42	34.0	84.91	9.00	(270 ppm)	1.27
Total Neutrals (I and II)	88.1	85.09	11.30	(78 ppm)	1.59	89-90	85.20	11.30	(103 ppm)	1.59
Pyrolics	3.36	83.75	8.29	1.93	1.19	2-3	--	--	2.0	--
Bases	7.52	70.87	7.25	1.51	1.01	8.26	--	--	1.65	--
Acids	2.74	82.20	9.13	1.31	1.33	1.39	--	--	1.60	--
Sum of Fractions	101.7	--	--	0.22	--	100-102	--	--	0.23	--

**TABLE 7**  
**COMPARISON OF PROPERTIES BETWEEN GAS OILS AND DISTACT DISTILLABLES**

	Heavy Vac Gas Oil A	Heavy Vac Gas Oil B	Resid B DISTACT distillate
%C <sub>A</sub> (by C-13 NMR)	21.8	24.9	25.0
Total N (ppm)	1540	2820	2700
Avg MW	400 ± 30 (by MS)	350 ± 30 (by MS)	570 (VPO)
Alumina ABN Yield (wt%, normalized)			
1. Neutrals	93	90	87
2. Pyrolics	0.49	0.88	3.3
3. Acids	3.5	5.0	2.6
4. Bases	3.0	4.0	7.3
5. Total polars (2 + 3 + 4)	7.0	9.9	13
N Concentration in ABN Fractions (Wt% observed):			
1. Neutrals	0.013	0.024	0.008
2. Pyrolics	3.0	3.2	1.9
3. Acids	2.3	3.2	1.4
4. Bases	1.3	0.82	1.6

TABLE 8

## CALCULATED AVERAGE MOLECULAR STRUCTURAL PARAMETERS OF RESID A DISTACT FRACTIONS

1. Calculated Structural Parameter				
Sample	# Condensed Aromatic Rings	NMR Cluster Wt	VPO MW	GPC MW
R <sub>1</sub>	5.4	749	1380	1500
O <sub>3</sub>	4.3	918	800	900
O <sub>4</sub>	3.4	838	500	500
O <sub>5</sub>	2.5	701	470	-
O <sub>6</sub>	1.6	526	400	450

2. Experimental Data							
Sample	H/C	C <sub>A</sub>	H <sub>a</sub>	H <sub>alpha</sub>	H <sub>methylene</sub>	H <sub>methyl</sub>	C <sub>methyl</sub>
R <sub>1</sub>	1.35	36.9	8.0	15.3	59.4	17.3	9.7
O <sub>3</sub>	1.51	26.8	5.5	11.2	63.3	20.0	11.6
O <sub>4</sub>	1.57	25.0	5.7	10.3	63.7	20.3	10.1
O <sub>5</sub>	1.59	23.4	5.3	11.2	62.0	21.5	9.4
O <sub>6</sub>	1.64	21.4	5.4	11.6	59.5	23.5	13.5

TABLE 9 PROPERTIES OF GPC CUTS OF RESID B ASPHALTENES

GPC Cut Number	1	2	3	4	5	6	7
H/C	1.09	1.09	-	1.14	1.13	1.07	-
GPC Number Avg. MW	5160	5020	3720	2410	1330	620	-
VPO Number Avg. MW	-	6830	-	2460	1370	-	-
Yield (wt%)	9.7	14.3	20.5	17.4	17.1	12.4	8.5
Elemental Composition (wt%) :							
C	83.72	84.23	-	84.30	84.16	84.08	-
H	7.60	7.66	-	8.00	7.90	7.52	-
N	1.13	1.11	-	1.01	1.02	1.16	-
S	6.37	6.49	-	6.18	6.09	5.96	-
O (by difference)	1.2	0.5	-	0.5	0	1.3	-
Metal Concentration (ppm) :							
Fe	134	29	34	87	35	320	-
Ni	228	130	122	127	144	450	-
V	590	490	490	530	490	1230	-
Ca	101	141	44	64	50	344	-
Zn	66	34	21	43	29	82	-
Total Metals	1120	830	711	850	750	2430	-
NMR Parameters							
C <sub>A</sub> (by C <sub>13</sub> -NMR)	51	48	-	47	47	53	-
Number of condensed aromatic rings	14	7.0	-	5.7	4.4	5.1	6.4
Cluster weight	1004	654	-	595	501	490	470

TABLE 10

## SUMMARY OF PROPERTIES OF HEAVY OIL COMPONENTS AS A FUNCTION OF BP

Chemical Properties	Vacuum Gas Oil (FHD-756)	1000+ Resid								
		DISTACT Distillables					DISTACT Bottom		Asphaltenes	
		960	1090	1220	1250	Total	Asphaltene Removed	> 1300°F		
190 BP (°F)	850									
Ave. MW	400	400	470	500	800	1380	800	500-600	1300-2400	4000-5000
% C <sub>A</sub> by NMR	22	21	23	25	27	37	32	53	47	48
Number of Condensed Aromatic Rings	1.5	1.6	2.5	3.4	4.3	5	5	5	4-6	7
Atomic H/C Ratio	1.7	1.64	1.59	1.57	1.51	1.31	1.4	1.07	1.13	1.09
Wt% S in fraction	-	2.9	3.6	3.9	4.3	6.2	6	6.0	6.1	6.5
Wt ppm Ni + V	< 1	1	12	80	130	490	410	1700	620	620
Wt% N in fraction	0.15	0.12	0.21	0.27	0.37	0.7	0.6	1.16	1.01	1.11
ABN Separation by Alumina LC										
Neutral Material :										
Wt% Aromatics	47			82			50-70		20-30	
Wt% Saturates	45			6			0.1		< 0.1	
Ave. MW	400			570			-		-	
Polar Materials (Acids Plus Bases) :										
Wt%	8			10-13			30-40		70-80	
Ave. MW	400			580-600			-		2000	