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High-temperature simulated distillation GC analysis of petroleum resids and their products from catalytic upgrading over Co–Mo/Al_2O_3 catalyst

K. Madhusudan Reddy, Boli Wei, Chunshan Song*

Fuel Science Program and Laboratory for Hydrocarbon Process Chemistry, Department of Materials Science and Engineering, The Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA

Abstract

Two petroleum resids and their products from catalytic upgrading were characterized by high-temperature simulated distillation using gas chromatography (HT-SimDis GC) with a capillary column. The atmospheric equivalent boiling points (AEBP) determined by the HT-SimDis GC method in this work reached an end point of 847°C (1557°F). This method successfully analyzed the AEBP distribution of an atmospheric resid and a vacuum resid as well as their products from catalytic hydroprocessing. The analysis of the AEBP distribution vs. reaction temperature revealed that catalytic upgrading not only produced lighter fractions but also created desirable changes in the remaining >540°C fractions. For the runs over a sulfided Co–Mo/Al_2O_3 catalyst, the yields of products with BP range of 540–700°C remained almost constant when the reaction temperature was within 350–400°C but decreased monotonically with further increasing reaction temperature up to 450°C. At 450°C, the 450–540°C fraction was also converted. The extent of catalytic hydrodesulfurization over Co–Mo/Al_2O_3 catalyst increased with temperature from 350 to 450°C.

Keywords: Simulated distillation; Gas chromatography; Petroleum resids; Characterization; Catalytic upgrading; Boiling point distribution

1. Introduction

Residues of petroleum distillation, also called resids, are referred to as the bottom of the barrel and include two types of distillation tower bottoms. The term 'atmospheric resid' describes the material at the bottom of the atmospheric distillation tower having a lower boiling limit of about 340°C; the term vacuum resid refers to the bottoms from vacuum distillation which has an atmospheric equivalent boiling point (AEBP) range above 540°C [1].

The main purpose of petroleum resid upgrading is to reduce the boiling points as well as to remove sulfur, nitrogen and metals. Hydroprocessing is one of the important ways of resid upgrading. It is necessary to characterize resids and their products with various techniques that indicate their compositional features. Because petroleum resids are complex mixtures that contain hundreds of compounds with high molecular weights, characterizing resids is a tedious and complicated task. Laboratory-scale distillation tests are time-consuming but widely used for determining the boiling point range of crude oils and their products [2]. However, the boiling point range that can be determined by

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*Corresponding author. Tel.: +1 814 8634466; fax: +1 814 8653075; e-mail: csong@psu.edu

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laboratory distillation operation is limited, particularly for resids.

Simulated distillation analysis by gas chromatography (SimDis GC) requires about 1 h each test. It achieved ASTM standard status in 1973 as test D2887. This test was revised in 1984, 1989 and 1993. ASTM D5307 was defined in 1992 for determining the crude oil boiling point range. However, these methods can only be applied to fractions with final boiling point up to 538°C (1000°F) [3,4]. Consequently, various techniques have been tested to determine the boiling point distribution of heavy resids. Padlo and Kugler studied SimDis by HPLC (high performance liquid chromatography) using an evaporative light scattering detector [5]. Bacaud et al. performed modeling based on SimDis GC to evaluate hydroprocessed resids [6] and Klein and co-workers used it as a part of their analytical data for resid structure modeling [7].

High-temperature simulated distillation using GC (HT-SimDis GC) has become possible recently with the development of thermally stable wide bore capillary columns. Some of the advantages of open tubular columns over packed columns are: better column stability and life, lower column bleed, faster analysis, elution of higher boiling petroleum fractions, compatibility with automated on-column injection, and improved reproducibility [8]. However, HT-SimDis GC has not been widely used, and no standard method is available for resids. We have established a method in our laboratory for HT-SimDis GC analysis of petroleum resids with AEBP end points of up to 847°C (1557°F). This paper presents our results on HT-SimDis GC analysis of two resids and their products from laboratory tests of catalytic hydroprocessing. The term ‘resid’ in the remainder of this paper refers to the feedstock, and the term ‘residue’ refers to the uneluted portion of the resid in HT-SimDis GC.

2. Experimental

2.1. *Solvent extraction*

Two petroleum resids, an atmospheric resid (AR) and a vacuum resid (VR) were used in this study which were obtained from Marathon Oil Company (as atmospheric resid #1, and vacuum resid #2, from Garyville Refinery). Their elemental compositions are as follows: for AR, C: 84.64; H: 11.14; S: 3.87; N: 0.23, O (by difference): 0.12 wt.%; and for VR, C: 83.20; H: 9.83; S: 5.01; N: 0.54, O (by difference): 1.42 wt.%. Asphaltenes, the hexane-insoluble but toluene-soluble fraction of the resid were estimated for AR and VR. To do this estimation, 4 g resid was dissolved in 400 ml hexane in an ultrasonic bath for 1 h and then filtered through a 0.45 μm (pore size) membrane filter. The solid on filter paper was dried and weighed as hexane insoluble (HI) material. A similar procedure was used with toluene to determine the toluene insoluble (TI). The amounts of asphaltenes in AR and VR were determined from the difference of hexane and toluene insoluble.

2.2. *High-temperature simulated distillation GC*

HT-SimDis GC was performed using a Hewlett-Packard Model 5890 II Plus GC with a flame ionization detector and temperature programmable cool on-column injector. On-column injection avoids sample discrimination and decomposition that can occur in heated inlets that rely on flash vaporization [8]. The injector temperature was always maintained 3°C higher than the column temperature. Each sample was injected with an automatic sampler to maximize reproducibility. Raising the column temperature above 400°C can cause a considerable drop in the capillary column flow rate. This is caused by the increased carrier gas at higher temperatures. To avoid this effect, the GC on column flow system is operated in a flow control mode with the carrier (He) flow constant (10.6 ml/min). The velocity of the carrier gas flow was 79.2 cm/s. A high-temperature aluminum-clad megabore capillary column (HT5 phase consisting of Carborane, 6 m length, 0.53 mm i.d., 0.78 mm o.d., and 0.1 μm film thickness; from SGE supplied by Supelco Inc.) was used for HT-SimDis GC analysis. A computer-based chromatography data system (Hewlett-Packard ChemStation software, B.02.04) was used for data acquisition. To obtain a sample area corrected for baseline drift and signal offset, the column compensation was performed and stored to do subtraction and give the right values. The SimDis expert software (V 5.0) provided by Separations Systems Co. was used for post-run data analysis of HT-SimDis.

Prior to injection, the samples were diluted with CS_2 to about 2 wt.%. High purity CS_2 was used as a solvent because of its miscibility with resids, low boiling point, and low response factor in the FID. The injection volumes were 1.0 μl. The calibration standard containing *n*-paraffins (C_5–C_{100}) was prepared by dissolving liquid *n*-paraffins mixture (C_5–C_{20}) and polywax (Polywax 655) in CS_2 under an IR lamp in a sealed vial. Compounds used a true boiling point references were reagent-grade chemicals obtained from commercial suppliers. High boiling point lube oil standard (supplied by Separation Systems) was used as a reference standard to check the HT-SimDis GC calibration; it was used as an external standard for estimating the uneluted portion (undistillable residue) of the resids and their products.

Four different sets of GC conditions were tested in screening analysis. After the conditions had been set to meet the performance requirements, the column was conditioned; the blank run was then conducted and the data stored for column compensation. Using the same conditions as for the blank run, an appropriate aliquot of the calibration mixture was injected to obtain a retention time vs. boiling point calibration. In general, the volume of the calibration mixture injected must be selected to avoid distortion of any component peak shapes caused by overloading the sample capacity of the column. Distorted peaks will result in erroneous retention times and hence in errors in the boiling point determination. The calibration curve (retention time of each peak vs. the corresponding boiling point of the component) should be essentially linear. Our calibration has been always linear in the range between C_{10} and C_{94} paraffin; the latter has a boiling point of 704°C. It was assumed that the calibration is linear beyond that point. Once a calibration is ready, it is then verified with reference standard. We have also measured boiling points of several types of pure model compounds (cycloalkanes, aromatics, heteroatom-containing compounds) and compared with their true boiling points.

Both external standard and real samples were prepared after allowing them to reach room temperature (if they were stored in a refrigerator) to make them homogeneous. The exact amounts were weighed and dissolved in given amounts of CS_2 in order to obtain about a 2 wt.% solution in CS_2.

The external standard and resid samples were analyzed separately using exactly the same conditions that were used in the blank and calibration runs. Exactly 1 μl of diluted samples and external standards were injected using the auto sample injector. With the total corrected cumulative area of the external standard and the samples, the residue (uneluted portion of the samples) was estimated using following equations:

$$W_E = \frac{M_E}{(M_C + M_E)}$$

where W_E=weight fraction of external standard, M_E=weight of external standard, and M_C=weight of solvent CS_2.

$$W_S = \frac{M_S}{(M_C + M_S)}$$

where W_S=weight fraction of resid sample, M_S=weight of resid sample, and M_C=weight of solvent CS_2.

$$\mathrm{ESAM} = 100 \times \left(\frac{A_S}{A_E}\right) \times \left(\frac{W_E}{W_S}\right)$$

where ESAM=eluted portion (distillable) of the resid sample in wt.%, A_E=cumulative GC peak area of external standard of 1 μl injection, and A_S=cumulative GC peak area of resid sample of 1 μl injection.

$$\mathrm{RES} = 100 - \mathrm{ESAM}$$

where RES=uneluted portion (residue) of the resid sample in wt.%.

Once the percentage of eluted portion of resid sample has been estimated, the boiling point distribution is calculated from the cumulative area at regular intervals of retention time. The IBP is defined as the temperature equivalent to the time when the first cumulative area is 0.5% of the total. The rest of the boiling point distribution is calculated from the cumulative area at a given time equivalent to the particular temperature and the tabulated percentage of sample boiling at the corresponding temperature.

2.3. *Hydroprocessing*

The hydroprocessing of AR and VR resids was performed in the absence and presence of commercial Co–Mo/Al_2O_3 catalyst criterion 344TL. Table 1 shows the properties of the catalyst. Prior to the catalytic test, the Co–Mo/Al_2O_3 catalyst was ground

Table 1
Properties of the criterion 344TL catalyst

Material type	Co–Mo/Al_2O_3
CoO (wt.%)	2.9
MoO_3 (wt.%)	13.5
Surface area (m^2/g)	208
Pore volume (cc/g)	0.53
Median pore diam. (Å)	110

Table 2
Boiling point range of different fractions

Fraction	Atmospheric equivalent boiling point	
	(°C)	(°F)
Light naphtha	IBP–130	IBP–266
Heavy naphtha	130–220	266–428
Atmospheric gas oil	220–340	428–644
Light gas oil	340–450	644–842
Heavy vacuum gas oil	450–540	842–1004
Super heavy gas oil	540–847	1004–1557
Nondistillable residue	>847	>1557

up and presulfided. The hydroprocessing was carried out in a 25 ml horizontal tubing bomb reactor loaded with 3 g of resid and 0.3 g of the catalyst under an initial hydrogen pressure of 6.9 MPa for 60 min. The reaction temperature range between 350°C and 450°C at intervals of 25°C. Details of catalyst sulfidation and hydroprocessing procedures are given elsewhere [9–11]. After reaction, the reactor was quenched in a cold water bath and products were collected in CS_2. The solid and liquid products were filtered. The insoluble solid product is referred to as coke. The liquids were analyzed by HT-SimDis GC. The SimDis analysis data were processed and reported according to the cut point ranges classified in Table 2 which is based on the classification proposed by Altgelt and Boduszinski [1] except that the FBP is 847°C instead of 700°C. Resid conversion was calculated from the fractions of >340°C and >540°C boiling point and the liquid yields.

3. Results and discussion

3.1. HT-SimDis GC method

To establish conditions for HT-SimDis GC analysis of resids and their products, analysis was performed at different GC conditions. Table 3 lists the four GC methods used. In the first two (TP1 and TP2), the lower detector temperature (350°C) was used. In TP2, the final oven temperature was higher but the heating rate lower than that TP1. The heating rate in TP3 was lower than that in TP4. Figs. 1 and 2 show the high-temperature gas chromatograms of resids AR and VR. Comparison of Fig. 1(B) (and Fig. 2(A)) with Fig. 1(A) indicates that at a low detector temperature and lower final column temperature (TP1) the GC is not sensitive enough to detect the heavy portion of resids. Increasing the final temperature and total time (in method TP2) improved the elution of heavy materials but the lower detector temperature presented problems. In third method TP3, we increased the detector temperature from 350°C to 435°C. The gas chromatograms using method TP3 (Fig. 1(C) and Fig. 2(B)) show that the high boiling portion of resid produces a significant second peak. To test for further improvement in the elution of resid, we increased the heating rate from 10°C to 15°C/min and the final holding time from 15.5 to 28.8 min in TP4. Comparing Fig. 1(D), with Fig. 1(C) or comparing Fig. 2(C) with Fig. 2(B) show that the increased heating rate reduced the time needed for resid elution. However,

Table 3
Different GC methods for HT-SimDis GC analysis

Method	Detector temperature	Column temperature program					
	(°C)	Initial temperature (°C)	Initial time (min)	Rate (°C/min)	Final temperature (°C)	Final time (min)	Total time (min)
TP1	350	40	1	15	355	18.0	40
TP2	350	40	1	10	425	15.5	55
TP3	435	40	1	10	425	15.5	55
TP4	435	40	1	15	425	28.8	60

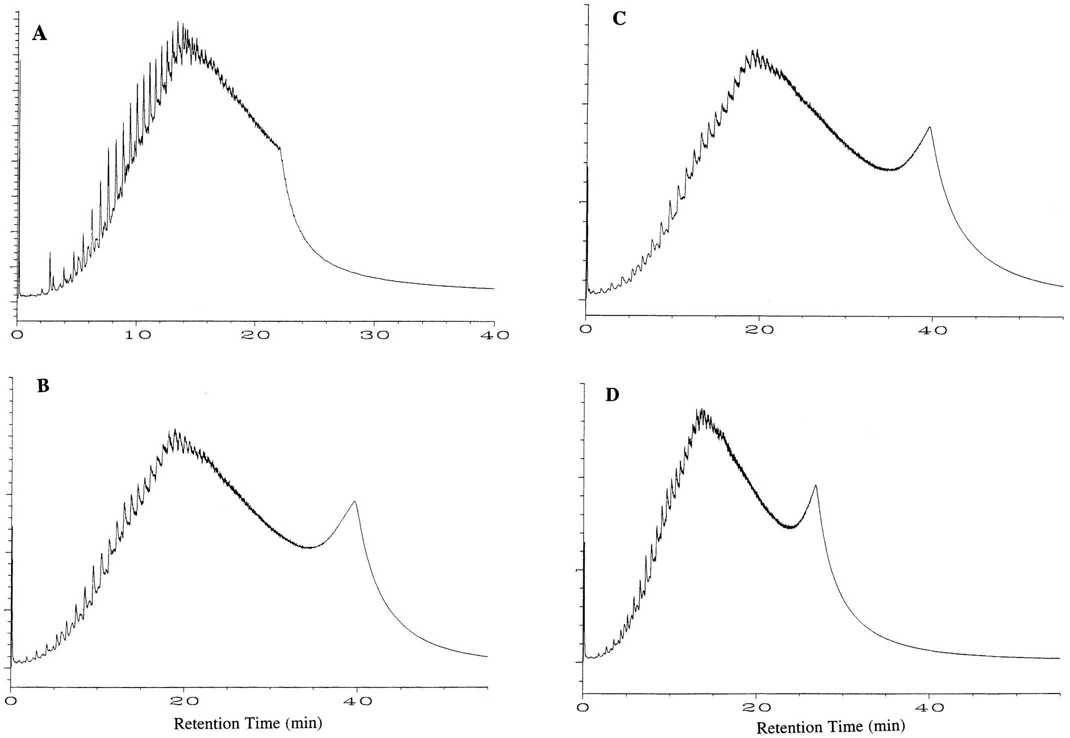

Fig. 1. HT-SimDis gas chromatograms of AR obtained using GC methods (A) TP1, (B) TP2, (C) TP3 and (D) TP4.

the higher heating rate gave poorer reproducibility during calibration. Table 3 and Figs. 1 and 2 indicate that method TP3 performed best in detector sensitivity, elution of high molecular weight compounds, reproducibility and the correct calibration. Hence this method was used for subsequent GC analysis.

To further confirm the general applicability of the method TP3, it was checked with a reference standard (high-temperature lube oil) and various model compounds. Fig. 3 shows the high-temperature gas chromatograms of the reference standard, AR and VR, respectively, along with calibration curves. It is clear from Fig. 3 that calibration curve is linear except lower paraffins (C_5–C_9). For the analysis of resids, it is necessary to calibrate to as high boiling point as possible. In this work it was possible to calibrate through C_{92} paraffin which has a boiling point of 704°C. The reference standard eluted within the range covered by the calibration curve (Fig. 3(A)). The atmospheric equivalent boiling point (AEBP) distribution obtained for the reference standard using our calibrated HT-SimDis is within ±3% of the values supplied by the vendor for that standard. Though a portion of the chromatograms for AR and VR were beyond the range of the calibration standard (Fig. 3(B) and (C)), the calibration was assumed to be linear through the range of resid elution.

In order to check the HT-SimDis applicability to various compounds, we also analyzed different types of pure compounds and estimated their boiling points using HT-SimDis method. For a pure compound the initial boiling point (where 0.5 wt.% sample is distilled) from HT-SimDis was taken as the estimated boiling point of that compound. Table 4 lists the estimated boiling points of the compounds. The boiling points derived from SimDis GC are consistent with the true boiling points within ±5% for most compounds, and ±7% for some compounds. It seems that the SimDis GC-derived boiling points tend to be slightly lower for many polycyclic aromatic compounds and polar compounds containing heteroatoms. However, the accuracy is considered to be

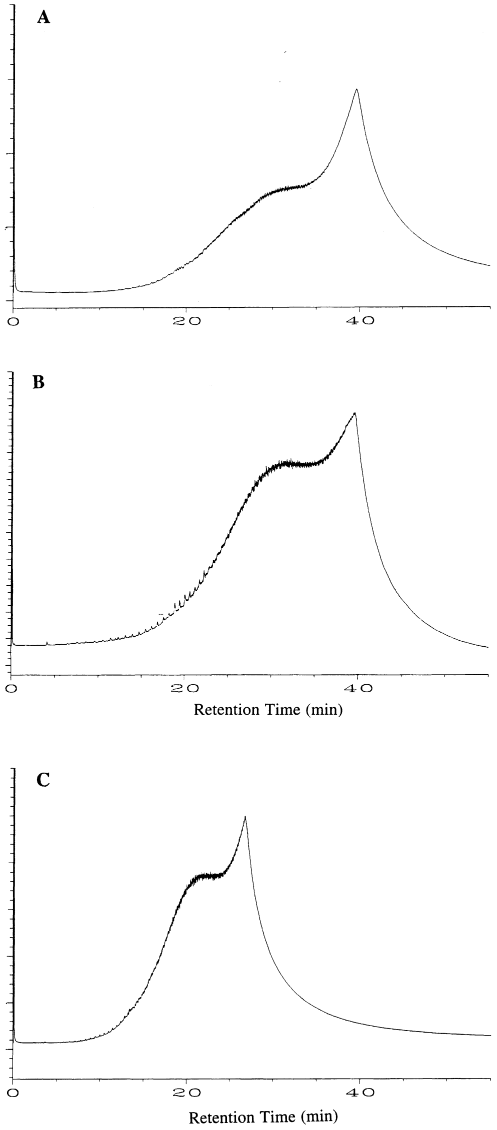

Fig. 2. HT-SimDis gas chromatograms of VR obtained using GC methods (A) TP2, (B) TP3 and (C) TP4.

acceptable for analyzing such complicated mixtures as resids.

3.2. *Analysis of resid feedstocks*

HT-SimDis gas chromatograms of AR and VR resids contain two major peaks (Fig. 3(B) and (C)). With VR, the second peak at high temperature is larger than that of AR, indicating that the VR has a larger high boiling fraction. The first peak and second peak in Fig. 3(B) (AR) correspond to AEBPs of about 450°C and 704°C, respectively; the two peaks in Fig. 3(C) (VR) correspond to AEBPs of about 608°C and 704°C, respectively.

Table 5 shows the AEBP distribution of AR and VR obtained using HT-SimDis, according to the boiling ranges shown in Table 2. The fractions with boiling point of >340°C (cut-off point for atmospheric distillation) in AR and VR are 93.9 and 99.1 wt.%, respectively. The fractions with AEBP's of >540°C (cut-off point for vacuum distillation) in AR and VR are 57.0 and 88.6 wt.%, respectively. Table 5 also shows the amount of residue (uneluted portion of the sample) estimated by HT-SimDis. The amounts of residue (with AEBP of >847°C) in AR and VR feedstocks are 16.5 and 21.6 wt.%, respectively. The amount of asphaltenes for AR and VR feeds were estimated from solvent extraction method and the values are 9.22 and 14.02 wt.%, respectively. It is interesting to note that these residue values are considerably higher than the asphaltene contents. AR is completely soluble in toluene, and VR only contains 0.12 wt.% toluene-insoluble material.

Figs. 4 and 5 illustrate the high-temperature gas chromatograms of feedstock, hexane soluble (HS) and hexane insoluble (HI) fractions of AR and VR, respectively. HT-SimDis gas chromatograms of feedstocks and HS fractions of AR (Fig. 4) and VR (Fig. 5) show two peaks but hexane insoluble (HI) fractions of both AR (Fig. 4(C)) and VR (Fig. 5(C)) resids show a single peak at high temperature. Essentially all HI is asphaltenes in these resids. We have found no literature report on HT-SimDis GC of asphaltene. The peak AEBP for asphaltene in AR (Fig. 4) is 704°C which corresponds to a GC oven temperature of 425°C. The majority of the asphaltene peak eluted between 32 and 48 min at 425°C which corresponds to an AEBP range of 620–840°C. A question that arises is, is this material asphaltene or is it the products of asphaltene decomposition. It is known that decomposition of asphaltene can occur in this temperature range [12]. It is difficult to clarify this issue for asphaltene because no standard reference is available. However, what we have established is that this peak is characteristic of the presence of very heavy materials, and this peak can disappear after upgrading. The

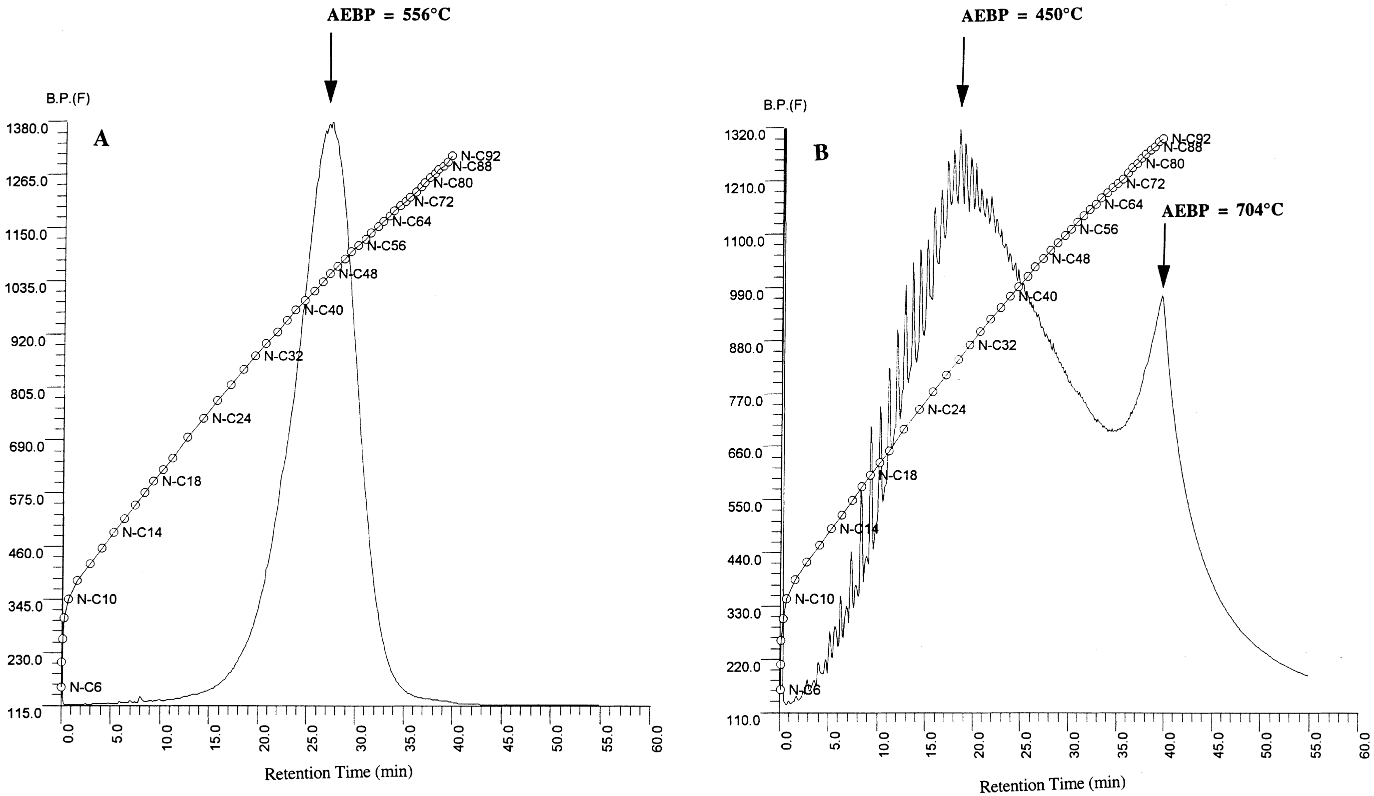

Fig. 3. HT-SimDis gas chromatograms of (A) high temperature lube oil (reference standard), (B) atmospheric resid (AR) and (C) vacuum resid (VR).

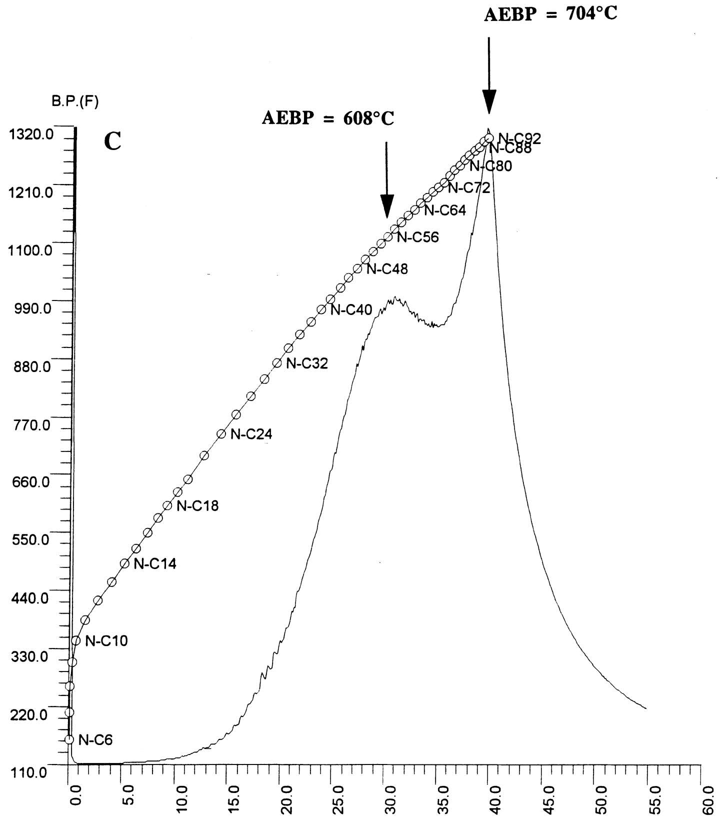

Fig. 3. (*Continued*)

eluted materials in Fig. 4(C) only represent 50.1 wt.% of the asphaltene fraction in AR. Similarly, the eluted materials in Fig. 5(C) represent only 39.7 wt.% of the HI (mostly asphaltene) in VR.

Another interesting feature is that the HS fraction of AR, the asphaltene-free materials, also displays the GC peak with AEBP of about 704°C (Fig. 4(B)) which is almost identical to that for asphaltene (Fig. 4(C)). This trend can also be observed for VR in Fig. 5. Apparently, asphaltene fractions contribute only partially to the second peak of the whole resids. These results show that asphaltene-free resids contain a significant amount of materials which have the same AEBP range as asphaltene. Such elutable heavy materials largely disappear in HT-SimDis GC of the upgrading products, as described below. HT-SimDis gas chromatograms of HI fractions (Fig. 4(C), Fig. 5(C)) and Table 5 clearly show that VR feed contains more high boiling fraction (second peak) and more asphaltenes compared to AR feed.

3.3. *Analysis of upgrading products*

Figs. 6 and 7 compare the high-temperature gas chromatograms of AR and VR feeds and their products obtained over Co–Mo/Al_2O_3 catalyst at 425°C, respectively. Compared to the AR feedstock, the chromatogram of products has more lighter components, and the second GC peak (due to heavy fraction of the feedstocks) eluting at higher temperature (Fig. 6) almost disappeared. This trend is more remarkable for VR (Fig. 7). Complete AEBP distribution of the liquid products, liquid yield, coke yield, and conversions of >340°C and >540°C fractions at different conditions are shown in Tables 6 and 7 for AR and VR, respectively. We have done several repeated

Table 4
Comparison of HT-SimDis derived boiling points with the true values of various compounds

Compounds	True boiling point		SimDis-BP		Deviation	
	(°C)	(°F)	(°C)	(°F)	(°C)	(% in °C)
Cycloalkanes						
Methylcyclohexane	101	214	104	220	3	3.3
trans-1,3-Dimethylcyclohexane	124	255	133	271	9	7.0
n-Hexylcyclohexane	221	430	223	434	2	1.8
cis-Decalin	193	379	197	387	4	2.3
trans-Decalin	185	365	194	381	9	4.8
Ethylcyclohexane	130	266	128	262	−2	−1.8
n-Propylcyclohexene	155	311	156	313	1	0.6
n-Butylcyclohexane	180	356	179	354	−1	−0.6
Aromatics						
Toluene	110	230	118	244	8	6.8
p-Xylene	139	282	140	283	1	0.4
Ethylbenzene	136	277	143	289	7	4.9
Naphthalene	218	424	218	425	0	0.1
Cyclohexylbenzene	239	462	240	464	1	0.4
2-Mehtylnaphthalene	241	466	237	459	−4	−1.6
1-Methylnaphthalene	240	464	227	441	−13	−5.2
2,6-Dimethylnaphthalene	262	504	275	527	13	5.0
1,5-Dimethylnaphthalene	266	511	278	532	12	4.4
Fluorene	298	568	291	556	−7	−2.2
Biphenyl	255	491	258	497	3	1.2
p-Terphenyl	389	732	383	721	−6	−1.6
Phenanthrene	336	637	320	607	−16	−4.8
Anthracene	342	648	340	643	−2	−0.7
Pyrene	395	743	382	719	−13	−3.4
Chrysene	447	837	418	784	−29	−6.6
Heteroatom-containing compounds						
Phenol	182	360	172	341	−10	−5.7
m-Cresol	203	397	197	386	−6	−3.2
2-Naphthol	285	545	284	543	−1	−0.3
Dibenzofuran	285	545	298	569	13	4.6
Quinoline	237	459	227	441	−10	−4.2
1.2.3.4-Tetrahydroquinoline	249	480	247	477	−2	−0.7
Acridine	346	655	349	659	3	0.7
Benzothiophene	221	430	219	426	−2	−0.8
Dibenzothiophene	332	630	317	603	−15	−4.5

Table 5
HT-SimDis GC analysis of AR and VR resid feedstocks

Feed	Atmospheric equivalent boiling point distribution (%)						
	IBP–220°C	220–340°C	340–450°C	450–540°C	540–700°C	700°C–FBP[a]	Residue[b]
AR	0.5	5.6	17.7	19.2	27.4	13.1	16.5
VR	0.3	0.6	2.0	8.5	43.1	23.9	21.6

[a] Final boiling point (FBP): ≤847°C.

[b] Residue: uneluted portion of the resid with AEBP of >847°C.

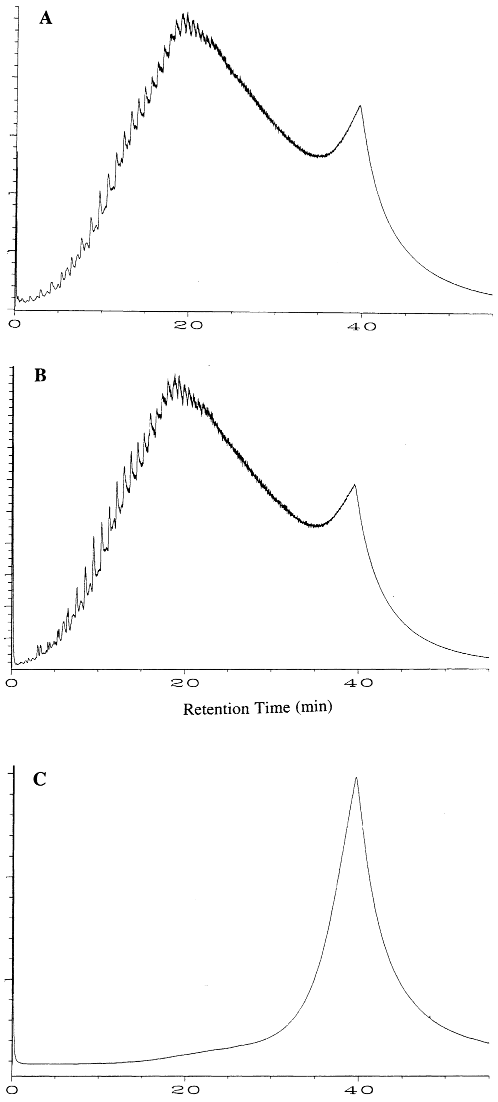

Fig. 4. HT-SimDis gas chromatograms of (A) AR, (B) hexane soluble fraction of AR and (C) hexane fraction of insoluble AR.

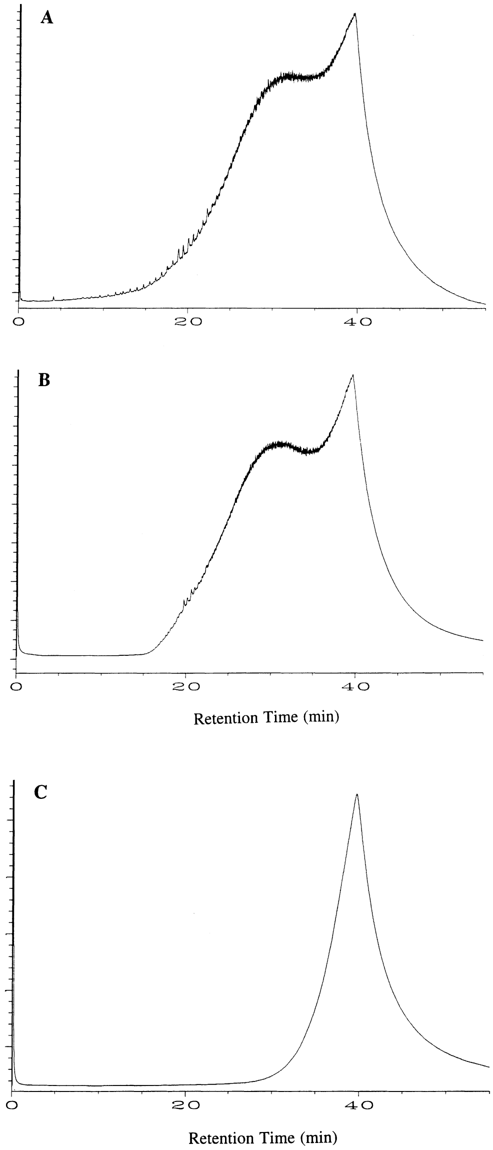

Fig. 5. HT-SimDis gas chromatograms of (A) VR, (B) hexane soluble fraction of VR and (C) hexane fraction of insoluble VR.

analyses for some samples to examine the reproducibility of the HT-SimDis analysis of upgraded products. Table 8 shows the good reproducibility of the AEBP distribution of AR, VR and their products from repeated analyses. AEBP distribution from Tables 6 and 7 reveals that both catalytic and noncatalytic upgrading of AR and VR produced lighter fraction but the extent of lighter fraction production varied with the type of feedstock and the temperature. Increasing the reaction temperature increased the conversion of >340°C and >540°C fractions both in the presence and absence of catalyst. However, the presence of catalyst has two positive effects: (1) more heavy materials (>847°C fraction) is converted, and (2) the coke formation is suppressed, particularly in the case of VR upgrading. Thermal runs produced

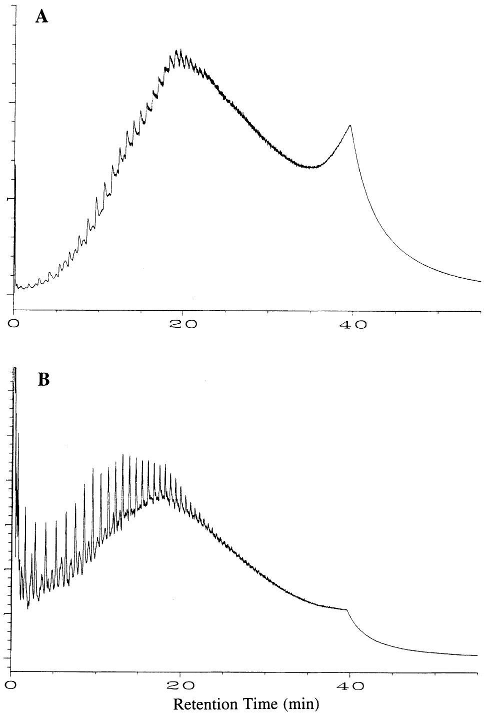

Fig. 6. HT-SimDis gas chromatograms of (A) AR feed and (B) product obtained over Co–Mo/Al_2O_3 (criterion 344TL) at 425°C.

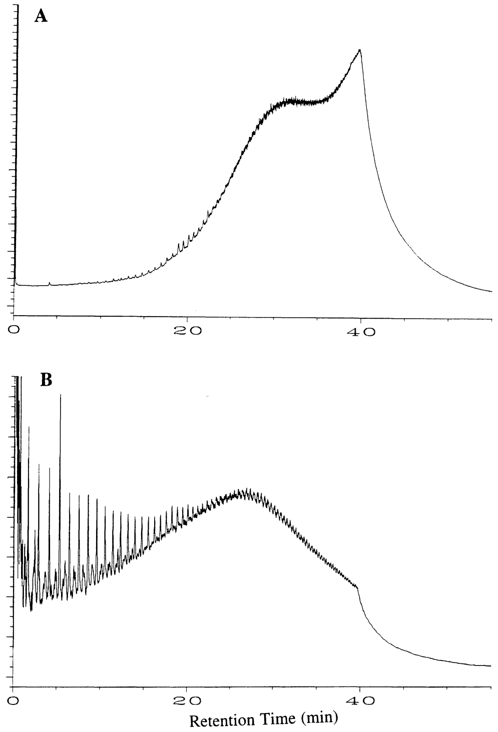

Fig. 7. HT-SimDis gas chromatograms of (A) VR feed and (B) product obtained over Co–Mo/Al_2O_3 (criterion 344TL) at 425°C.

larger amounts of coke with lower liquid yield at high temperature of 450°C which indicate condensation of reactive fragments in the absence of catalyst. In the case of VR resid upgrading, more of the >540°C fraction is converted both in catalytic and noncatalytic runs, compared to those of AR resid. Consequently the fractions between IBP–220°C and 200–340°C increased significantly during the hydroprocessing of VR resid at 425–450°C.

Fig. 8 clearly illustrates that the reaction temperature has a significant influence on product distribution, particularly on >540°C fractions. At <400°C, there is no significant change in >540°C fractions. But an increase in temperature from 400°C to 425°C led to significant conversion of 540–700°C AEBP materials to lighter fractions (<450°C). This indicates that increasing the reaction temperature causes the production of large amounts of lighter fraction (<540°C) at the expense of heavier fractions (>540°C). When the temperature is further increased to 450°C, both the >540°C fraction and the 450–540°C fraction converted further. These results indicate that in hydroprocessing of VR, the temperature required to activate >540°C fraction is about 425°C, whereas 450–540°C fraction is activated at about 450°C.

Reduction in boiling points is also accompanied by desulfurization during resid upgrading. Fig. 9 demonstrates the effect of temperature on sulfur removal in hydroprocessing of VR in the presence and absence of Co–Mo/Al_2O_3 catalyst. Reaction temperature has a significant effect on desulfurization, particularly in the presence of catalyst. Unlike the AEBP distribution, the extent of catalytic desulfurization increased almost monotonically with increase in temperature from 350°C to 450°C. This trend is different from those observed for hydrodesulfurization of distillate fuels, where reaction temperature is typically between 350°C and 400°C.

It appears that catalytic hydrodesulfurization of resids also depends on thermally driven hydrocracking reactions. In other words, the C–C bond cleavage reactions are largely thermally driven in the catalytic

Table 6
HT-SimDis GC analysis of hydroprocessed AR resid over Co–Mo/Al_2O_3

Expt. ID	Catalyst	Reaction temperature (°C)	Atmospheric equivalent boiling point distribution (%)							Liquid yield (wt.%)	Coke yield (wt.%)	Conv. of fractions (%)	
			IBP–220°C	220–340°C	340–450°C	450–540°C	540–700°C	700°C–FBP[a]	Residue[b]			>340°C	>540°C
1	None	375	0.9	6.5	18.6	19.5	28.1	13.4	13.0	97.2	0.1	4.1	0.4
5	None	400	1.0	9.6	20.8	19.3	24.6	10.6	14.1	95.5	0.2	9.1	11.5
7	None	425	12.3	19.1	21.1	13.2	13.7	6.1	14.5	97.7	0.4	28.6	37.0
27	Co–Mo/Al_2O_3	375	0.7	7.0	19.9	20.3	28.2	12.9	11.0	97.2	0.1	4.4	4.8
20	Co–Mo/Al_2O_3	400	1.1	8.1	19.8	19.3	24.9	10.8	16.0	97.6	0.1	5.6	5.2
21	Co–Mo/Al_2O_3	425	5.4	13.7	22.7	18.5	19.9	7.1	12.7	94.8	0.2	18.3	29.3

[a] Final boiling point (FBP): ≤847°C.

[b] Residue: uneluted portion of the resid with AEBP of >847°C.

Table 7
HT-SimDis GC analysis of hydroprocessed VR resid over Co–Mo/Al_2O_3

Expt. ID	Catalyst	Reaction temperature (°C)	Atmospheric equivalent boiling point distribution (%)							Liquid yield (wt.%)	Coke yield (wt.%)	Conv. of fractions (%)	
			IBP–220°C	220–340°C	340–450°C	450–540°C	540–700°C	700°C–FBP[a]	Residue[b]			>340°C	>540°C
40	None	400	2.4	4.4	7.1	12.8	39.7	18.9	14.7	97.3	0.2	8.5	16.0
31	None	425	6.2	13.0	14.2	13.4	21.3	7.7	24.2	95.2	1.9	22.4	40.3
37	None	450	8.6	27.2	21.5	12.5	13.3	6.0	10.9	77.6	13.6	49.8	72.4
47	Co–Mo/Al_2O_3	350	0.9	3.5	4.4	10.0	42.4	21.4	17.4	97.6	0.1	5.8	6.6
46	Co–Mo/Al_2O_3	375	1.2	3.6	4.4	10.2	40.0	20.4	20.2	97.2	0.1	6.6	7.7
42	Co–Mo/Al_2O_3	400	2.6	5.0	7.0	12.9	39.8	18.1	14.6	97.0	0.2	9.6	17.2
33	Co–Mo/Al_2O_3	425	5.6	10.7	14.3	17.2	29.1	9.5	13.6	94.6	0.4	20.1	41.8
38	Co–Mo/Al_2O_3	450	13.9	22.9	20.6	14.0	15.3	6.1	7.2	85.4	1.5	45.6	71.2

[a] Final boiling point (FBP): ≤847°C.

[b] Residue: uneluted portion of the resid with AEBP of >847°C.

Table 8
Reproducibility check for HT-SimDis GC analysis of AR and VR feedstocks and some VR products

Expt. ID	Temperature	Atmospheric equivalent boiling point distribution (%)						
	(°C)	IBP–220°C	220–340°C	340–450°C	450–540°C	540–700°C	700°C–FBP[a]	Residue[b]
AR	—	0.5	5.6	17.7	19.2	27.4	13.1	16.5
AR	—	0.6	5.4	17.5	19.2	27.3	13.4	16.6
VR	—	0.3	0.6	2.0	8.5	43.1	23.9	21.6
VR	—	0.4	0.6	2.0	8.6	44.4	25.4	18.6
37/A	450	9.2	28.4	22.2	12.4	12.4	4.8	10.6
37/B	450	8.9	27.5	21.9	12.6	13.0	5.3	10.8
37/C	450	8.6	27.5	21.5	12.5	13.3	5.7	10.9
31/A	425	6.7	12.1	13.8	13.4	20.5	8.6	24.9
31/B	425	6.7	11.7	13.6	13.4	20.7	9.4	24.5
31/C	425	6.2	13.0	14.2	13.4	21.3	7.7	24.2
46/A	375	0.7	3.0	4.3	9.9	38.9	18.4	24.8
46/B	375	1.2	3.6	4.4	10.2	40.0	20.4	20.2

[a] Final boiling point (FBP): ≤847°C.
[b] Residue: uneluted portion of the resid with AEBP of>847°C.

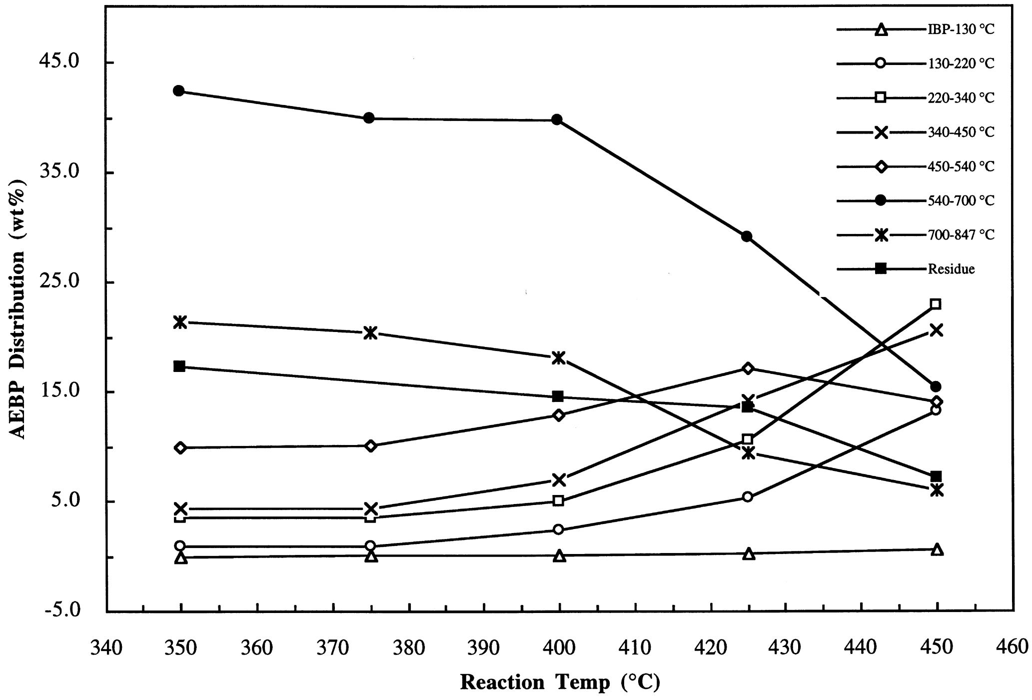

Fig. 8. Effect of temperature on VR hydroprocessing over Co–Mo/Al_2O_3 catalyst. The residue fraction refers to the uneluted resid products with AEBP of >847°C.

upgrading. The catalyst has two roles. First, it promotes hydrogen transfer to produce stable molecules and suppress coke formation. Second, it enhances the desulfurization of relatively smaller molecules derived from the resids. In the noncatalytic reaction, coke formation is significant at 450°C (Table 7).

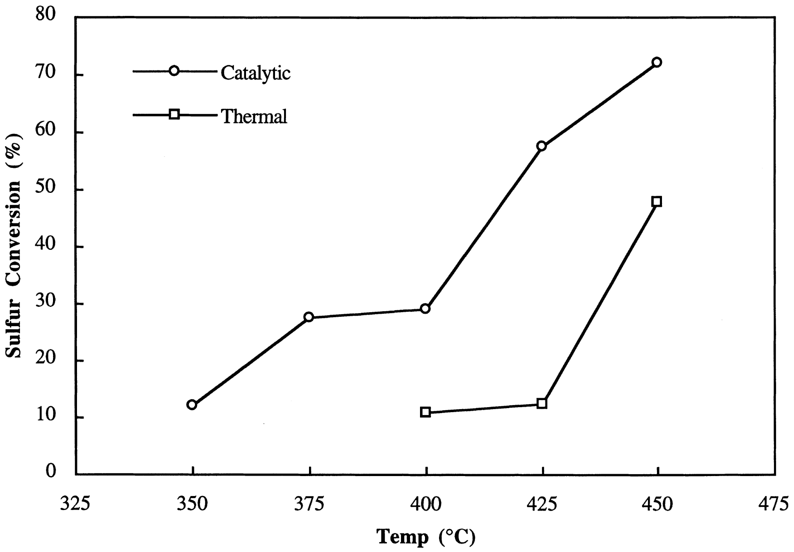

Fig. 9. Effect of temperature on sulfur conversion by HDS during VR hydroprocessing in the presence and absence of sulfided Co–Mo/Al_2O_3 catalyst.

4. Conclusions

For simulated distillation of heavy petroleum fractions using GC, it is important to use the right GC conditions. After screening tests at various GC conditions in this work, a HT-SimDis GC method has been established which can be used to determine AEBP distributions up to 847°C. It has been successfully applied for analyzing the AEBP distribution of atmospheric resid (AR) and a vacuum resid (VR) as well as their products from catalytic hydroprocessing.

HT-SimDis GC analysis of AR and VR feedstocks clearly indicated the difference in AEBP distribution between the two feedstocks which is partially responsible for different levels of upgrading. Such analysis also revealed that both thermal and catalytic hydroprocessing of AR and VR caused changes in AEBP distribution of higher boiling fractions (>450°C AEBP). For the runs over a sulfided Co–Mo/Al_2O_3 catalyst, the yields of products with AEBP range of 540–700°C remained almost constant between reaction temperatures of 350–400°C but decreased monotonically on increasing reaction temperature to 450°C. At the high reaction temperature (450°C), the 450–540°C fraction is also converted significantly. The extent of catalytic hydrodesulfurization over Co–Mo/Al_2O_3 catalyst increased monotonically with an increase in reaction temperature from 350°C to 450°C.

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