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Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction

Technical Progress Report

July - September 1996

(Approved)

Yoshiharu Yoneyama, Boli Wei, Kondam Madhusudan Reddy,
Chunshan Song, and Harold H. Schobert

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ABSTRACT

This quarterly report describes our recent work on two related subjects: 1) effect of dispersed molybdenum catalyst precursor and the influence of water addition on C-O bond cleavage, aromatic hydrogenation and hydrodeoxygenation under coal liquefaction conditions, and 2) the effect of dispersed molybdenum catalyst precursor on the molecular weight reduction and desulfurization of petroleum resids related to coal/petroleum resids coprocessing.

There are many connecting linkages in coal structures, and the aromatic C-O and aromatic-aliphatic C-C bonds are believed to be important linkages between aromatic moieties of coal structures. Therefore in order to increase the conversion of coal to liquids, it is necessary to cleave these connecting linkages. Here we report on the effect of dispersed Mo catalysts and water addition on hydrogenation and C-O bond hydrogenolysis of 2,2'-dinaphthyl ether, abbreviated as DNE. In our recent work we found that the addition of water has a strong promoting effect on low-severity catalytic coal liquefaction using in-situ generated MoS_2 catalyst. In order to clarify the role of water, model reactions of 2,2'-dinaphthyl ether (DNE) were carried out using ammonium tetrathiomolybdate (ATTM) as catalyst precursor in the absence and presence of H_2O or D_2O. The addition of water to the non-catalytic runs of DNE has no effect at 350 - 400 °C, but the use of ATTM increased DNE conversion. Addition of H_2O significantly promoted DNE conversion and the yields of C-O bond cleavage products as well as their hydrogenation. In order to clarify the effect of water on the catalytic activity, two-step reactions were carried out. Catalysts were prepared from the runs using ATTM with and without water, and then DNE was hydrogenated with and without water. After the preparation of catalyst from ATTM and water, the removal of water prior to the reaction causes complete conversion of DNE; on the other hand, after the preparation of catalyst from the run using ATTM alone, an addition of water decreases the conversion of DNE. These results suggest that addition of proper amount of water is effective for the in-situ generation of active catalyst for hydrogenation of DNE, but water itself does not have positive effect on DNE conversion.

It is very interesting to note that the model compound studies clearly established that there is a strong promoting effect of water on the catalytic runs at relatively low temperatures using dispersed ammonium tetrathiomolybdate as catalyst precursor.

With an ultimate goal of exploring the potential of dispersed and supported catalysts for coal/resids coprocesssing process, we conducted a preliminary study on resid upgrading using both water-soluble and oil-soluble precursors of Mo sulfide catalysts as well as laboratory-prepared and commercial supported bimetallic catalysts. This report presents a summary on upgrading of two petroleum resids (atmospheric and vacuum resids) in terms of boiling point reduction and hydrodesulfurization. High-temperature simulated distillation (HT-SimDis) GC analysis was adopted to evaluate the resids and their hydroprocessing products from laboratory batch reactors. Effect of GC conditions was examined using three different temperature programs and two detection temperatures. Best conditions were identified for heavy hydrocarbons in the resids with boiling point up to about 750°C (1382°F). The resids were hydrotreated under a cold hydrogen pressure of 6.9 MPa H_2 in the temperature range of 350-450°C with or without catalyst. Four Mo-based supported and unsupported catalysts were tested and the products were analyzed by both H-T SimDis and sulfur analyzer. The SimDis results indicate that through proper hydrotreating the heavy resids can be upgraded to light oils. Different Mo-based catalysts showed different behavior for molecular weight reduction and for desulfurization of resids.

TECHNICAL PROGRESS

1. Effect of In-Situ Generated MoS_2 Catalyst and Influence of Water Addition on Hydrogenation and C-O Bond Cleavage of 2,2'-Dinaphthyl Ether

INTRODUCTION

In our recent work, we found a strong promoting effect of water on low-severity catalytic coal liquefaction using molybdenum sulfide catalyst in-situ generated from ammonium tetrathiomolybdate (ATTM): addition of water increased the conversion of Wyodak coal using ATTM as a catalyst precursor at 350 °C from 29.5 to 66.5 wt% [1]. Initially, this strong promoting effect of water was surprising to us, because it has been shown that better drying method for moisture removal results in higher coal conversion in catalytic liquefaction using molybdenum sulfide catalyst [2]. It was also observed that addition of water to catalytic coal hydroliquefaction has negative effect [3-5]. On the other hand, water addition to non-catalytic coal conversion reactions and some model reactions has been shown to have positive impacts [6-10]. More recently, it has been reported that ether compounds such as 1-phenoxynaphthalene and 9-phenoxyphenanthrene cleave in water at 315 °C, and this cleavage is enhanced at higher temperature; since water becomes a stronger acid as temperature increased, this cleavage reaction proceeds through ionic process [9,10].

In the present study, in order to clarify the role of water in catalytic hydroliquefaction of coal, we carried out hydrogenation and hydrogenolysis of 2,2'-dinaphthyl ether (DNE) using ATTM as a catalyst precursor in the absence and presence of H_2O or D_2O. There are many connecting linkages in coal structures; the aromatic C-O and aromatic-aliphatic C-C bonds are believed to be important linkages between aromatic moieties of coal structures. Therefore, in order to increase the conversion of coal to liquids, it is necessary to cleave these connecting linkages. Coal structures have not been clarified at the molecular level. The use of coal-related model compounds is suitable for understanding fundamental chemistry. The products from the hydrogenation of model compounds can be easily identified by GC/MS. DNE has been shown to be thermally unreactive in the absent of catalyst, but its conversion is enhanced by some metal sulfide catalyst [11]. Here we used DNE to investigate the effect of the addition of water on cleavage of ether-linkages and on hydrogenation of aromatic rings using ATTM under the conditions of coal liquefaction.

EXPERIMENTAL SECTION

Preparation of Catalyst Precursor

Ammonium tetrathiomolybdate (ATTM) were purchased from Aldrich, and 2,2'-dinaphthyl ether (DNE) from TCI America. DNE and ATTM were used without further purification. It was noted in previous work in this laboratory that long-time storage of ATTM in reagent vials in air may lead to degradation of the reagent, which results in deviations in the activity of in-situ generated MoS_2 catalyst from different bottles of ATTM reagent. In this work, a bottle of newly purchased ATTM was used in all the experiments on DNE runs, and the reagent bottle was stored in a refrigerator in order to minimize oxidative degradation.

Model Compound Reactions

A horizontal tubing bomb microautoclave reactor with a capacity of 25 mL was loaded with ca. 0.216 g DNE, 1 wt% catalyst precursor (1 wt % Mo based on DNE) and 1.47 g solvent (tridecane). When water was added, the weight ratio of H_2O to DNE was 0.56, unless otherwise mentioned. The reactor was purged four times with H_2 and then pressurized with 6.9 MPa H_2 at room temperature for all experiments. A preheated fluidized sand bath was used as the heating source, and the horizontal tubing bomb reactor was vertically agitated to provide mixing (about 240 strokes/min). After the reaction the hot tubing bomb was quenched in a cold water bath. The contents were washed with 30 - 40 mL acetone through a low speed filter paper for qualitative and quantitative GC analysis of the filtrate. Two-step reaction was also carried out in a similar manner as described above, except that the active MoS_2 catalyst was prepared first using ATTM with and without H_2O in the first-step reaction, and subsequently, the reactor was opened, and DNE was then added into the reactor. DNE was treated with and without H_2O as the second-step reaction.

The products were identified by GC-MS using a Hewlett-Packard 5890 II GC coupled with a HP 5971 A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 50% phenyl 50% methylpolysiloxane with a coating film thickness of 0.25 µm. For quantification, a Perkin Elmer 8500 GC with flame ionization detector and the same type of column (DB-17) was used. Both GC and GC-MS were programmed from 80 to 280 °C at a heating rate of 4 °C/min and a final holding time of 8 min. The response factors for 5 of the products were determined using pure compounds.

Determination of Response Factor

Response factors of the components were calculated equation shown below.

Response factor = $[(A_j/M_j) / (A_{isd}/M_{isd})] \times 1.05$;

Mass of internal standard (n-Dodecane): M_{isd}
Peak Area (area%) of internal standard in GC: A_{isd}

Mass of component j: M_j
Peak Area (area%) of component j in GC: A_j

GC analysis was carried out under the conditions shown below;
Injection volume: 1.0µl
Split or Spilitless: Split

Injection Temperature: 280 °C
Detector Temperature: 290 °C

Initial Temperature: 80 °C
Rate of Heating: 4 °C/min.
Final Temperature: 280 °C
Holding Time: 10 min.

When yields of the products are calculating by using response factor, the recovery of the products were sometimes low about from 90 to 95 wt%. Therefore the effect of products concentration in solution on the response factor is investigated. The response factor of the product except for DNE do not change with changing the concentration in solution, but the response factor of and DNE changes. Figure 1 shows the relationship between the response factor and the peak height of DNE in GC chromatograms. At lower concentration than 50 µV of peak height of DNE, the response factor follows equation (1), and At higher than 50 µV of peak height, it follows equation (2).

$y = 8.91 \times 10^{-3}x + 0.691$ (1)

$y = 9.54 \times 10^{-4}x + 0.5579$ (2)

So the response factor of DNE was calculated by these equations.

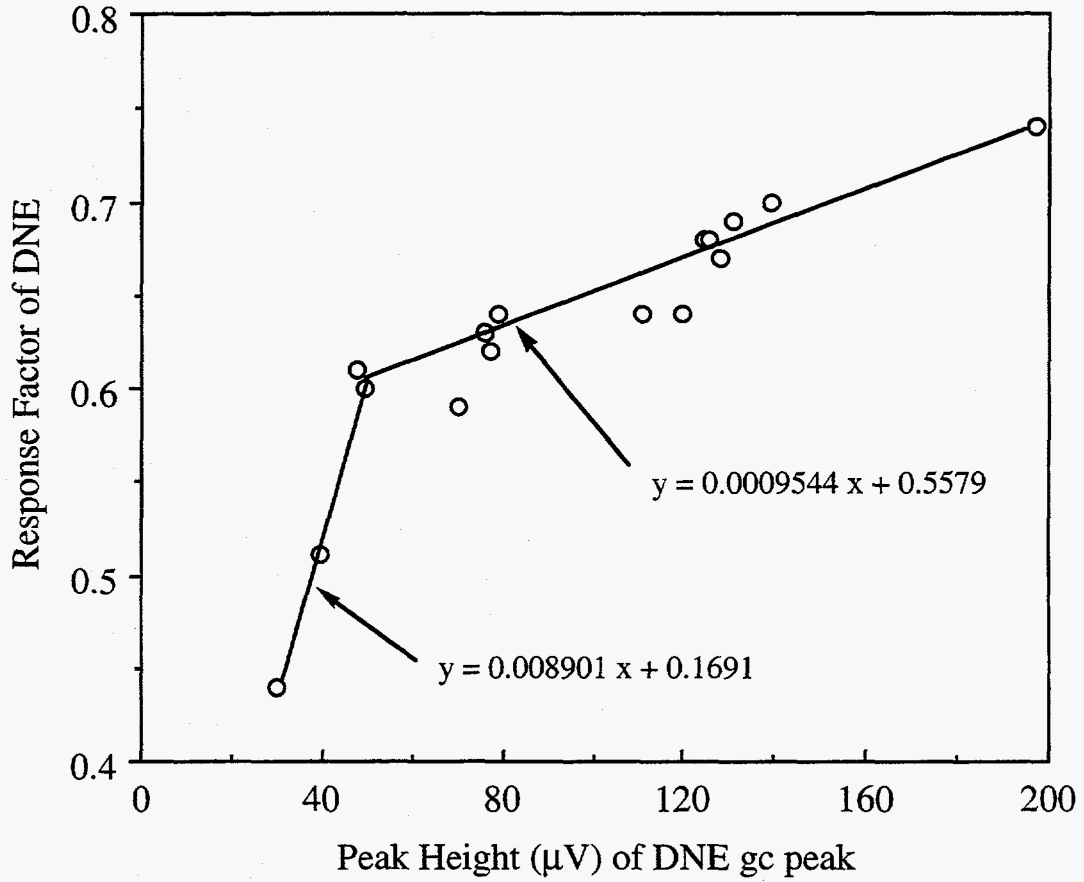

Fig.1 Relationship between gc response factor of dinaphthyl ether (DNE) and DNE peak height in gas chromatogam (DNE concentration in solution)

RESULTS AND DISCUSSION

One-Step Reaction

Table 1 shows the results of non-catalytic and catalytic runs of DNE with in-situ generated dispersed MoS_2 catalysts at 350, 375 and 400 °C. Without ATTM, the conversions of DNE are very low, even at 400 °C. Adding water alone seems to inhibit the conversion of DNE completely. However, in the presence of ATTM conversions are significant. An addition of water to the runs with ATTM substantially increase the conversion of DNE. Upon addition of water to the catalytic runs, the conversion of DNE increases from 46.0 % to 83.8 % at 350 °C. The principal products are tetralin, naphthalene, 2-naphthol, 5,6,7,8-tetrahydro-2-naphthol, octahydroDNE, and tetrahydroDNE. Formation of these products suggests that both the ether linkage cleavage reaction and hydrogenation of aromatic rings occur simultaneously. Because the yield of tetralin is higher for the runs with added water than for those without water, the hydrogenation of aromatic ring prevails in the run with water and ATTM.

Table 1 Effect of addition of H_2O on reactions of DNE at 350-400 °C under 6.9 MPa H_2.

Run #	16	17	15	19	18	20	7	6	8	5	3	4
Catalyst Precursors	None	None	None	H_2O	H_2O	H_2O	ATTM	ATTM	ATTM	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O
Temperature (°C)	350	375	400	350	375	400	350	375	400	350	375	400
DNE Conversion (mol %)	0.7	0.5	4.6	0.0	0.0	0.0	46.0	86.4	82.4	83.8	95.2	94.2
Products (mol %)												
Tetralin		0.7	5.4				31.4	70.9	66.7	72.7	106.1	109.1
Naphthalene		0.3	2.0				33.1	74.1	73.4	57.1	66.2	70.8
5,6,7,8-Tetrahydro-2-naphthol							8.0	6.2	3.6	8.1	9.5	6.0
2-Naphthol							2.2	4.7	12.6	3.4		
OctahydroDNE			0.3				1.3	2.0	1.0	2.5	2.2	
TerahydroDNE	0.6		0.6				7.4	6.5	3.2	10.6	2.1	1.2

In order to clarify the role of water, DNE was hydrogenated with ATTM and D_2O. Because aryl ethers cleave in H_2O at high temperature above 315 °C through ionic mechanism [5], this ionic effect of H_2O on the cleavage of C-O bond in DNE is investigated. Even though water alone has inhibition effect on conversion of DNE as described above. Table 2 represents the results of catalyst run of DNE with dispersed catalysts and H_2O or D_2O at 350, 375 and 400 °C. Comparing the results using H_2O and D_2O, the conversions of DNE are almost the same in each pair of corresponding runs. There are no apparent isotopic effect on the conversion of DNE and the yields of the products. The results of GC/MS analysis indicate that the products and recovered DNE contained a few deuterium atom, and the fragmentation of mass spectra of the products indicate that deuterium atoms were introduced into the products unselectively. These results show that the hydrogen from water has a little effect on the conversion of DNE. In other words, we have found no clear evidence that H_2O enhanced ether bond cleavage: the ionic effect of water on cleavage of ether-linkage in DNE is not significant.

Table 2 Catalytic reactions of DNE using ATTM and H_2O or D_2O at 350-400 °C under 6.9 MPa

Rnu #	29	5	32	3	27	4
Catalyst	ATTM + D_2O	ATTM + H_2O	ATTM + D_2O	ATTM + H_2O	ATTM + D_2O	ATTM + H_2O
Temperature(oC)	350	350	375	375	400	400
Conversion (mol%)	82.9	83.8	95.5	95.2	95.6	94.2
Compound identified (mol%)						
Tetralin	68.8	72.3	106.5	106.1	106.5	109.1
Naphthalene	59.7	57.2	71.2	66.2	64.7	70.8
5,6,7,8-Tetrahydro-2-naphthol	7.9	8.0	9.0	9.5	6.6	6.0
2-naphthol	2.2	3.2			1.1	
OctahydroDNE	2.4	3.1	0.7	2.2	1.1	
TetrahydroDNE	11.2	11.3	1.5	2.1	1.2	1.2

Two-Step Reaction

As shown in Tables 1 and 2, the conversion of DNE increases with an addition of water. In order to clarify the role of addition of water on the hydrogenation of DNE further, two-step reaction was carried out. In the first-step, the Mo sulfide catalyst was prepared from decomposition of ATTM in the presence and the absence of water at 350, 375 and 400 °C under hydrogen pressure for 30 min. Subsequently the reactor was quenched, vented, and opened to allow the loading of DNE followed by purge and repressurization with H_2. The hydrogenation of DNE, as the second-step, was carried out with and without H_2O at 350 °C under hydrogen pressure for 30 min. Table 3 shows the results of the two-step reactions. Using the catalyst prepared from ATTM alone at 350, 375 and 400 °C, the conversions of DNE are almost the same at 64-67 %: the activities of the catalysts are very similar. However, highly active catalysts are generated from ATTM with added H_2O, the conversion of DNE is the largest at 375 °C: the catalyst prepared at 375 °C is most active. This result is as same as our previous one[12]. After the preparation of catalyst, the addition of water decreases the conversion of DNE. For example the conversion of DNE decreased from 64.4 % to 32.9 % at 350 °C (first-step) after the addition of water to the second-step run. In addition, after the preparation of catalyst from ATTM and water at 350 °C complete removal of water caused about 100 % conversion of DNE at 350 °C at the second-step. These results suggest that water itself does not have promoting effect on hydrogenation of DNE, but that it is effective for the preparation of good catalyst for hydrogenation and bond cleavage of DNE.

Table 3 Two-step reactions of DNE under 6.9 MPa H_2.

Experiment #	44	48	49	41	42	51	68	67	50	96*
Temperature(°C) 1st	350	375	400	350	375	400	350	375	400	350
Temperature(°C) 2nd	350	350	350	350	350	350	350	350	350	350
First Catalyst	ATTM	ATTM	ATTM	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O	ATTM	ATTM	ATTM	ATTM + H_2O
Second Addition	None	None	None	None	None	None	H2O	H2O	H2O	None
Conversion (mol %)	64.4	66.7	66.0	82.7	96.0	76.9	32.9	29.7	41.2	97.0
Products (mol%)										
Tetralin	49.1	46.9	44.7	58.6	76.5	53.1	26.8	22.9	31.9	89.6
Naphthalene	67.5	72.6	72.6	79.5	85.1	75.9	26.6	25.5	39.5	104.4
Tetrahydronaphthol	0.8	0.6	1.0	1.4	1.6	4.2	1.2	0.6	0.7	
2-naphthol	0.8	0.6	1.0	0.4	0.1	2.2	1.6	0.8	1.0	
OctahydroDNE	0.3	0.3	0.4	0.8	2.1	0.7	0.2	0.2	0.2	
TetrahydroDNE	5.1	6.1	6.0	12.0	12.2	8.5	4.6	4.6	4.4	

* After the first-step reaction, water was completely removed by venting at 200 °C for 35 min., prior to the addition of DNE for second-step reaction.

Hand-Shaking Effect

While carrying out two-step reactions, we found a strange hand-shaking effect on the conversion of DNE: before starting a second-step run, a reactor which contained DNE was shook by hand above three hundred times, and the conversion of DNE increased. As shown below, because with below one hunderd times hand-shaking the conversion of DNE was still low, we shook the reacter above three hundred times. Table 4 shows the results of the hand-shaking effect. In all runs, the conversions of DNE are higher with hand-shaking than without hand-shaking and with one hundred times hand-shaking: the conversion of DNE improves from 10 % to 40% with hand-shaking for all runs. Without hand-shaking we cannot find the relationship between the conversion of DNE and temperature for catalyst preparation using only ATTM (first-step), but with hand-shaking it is clear that the conversions at 350, 375, 400 °C is almost the same. Therefore we used the hand-shaking for all two-step reactions described in Table 3.

Table 4 Hand shaking effect between first and second reactions on conversion of DNE and yields of products.

Experiment #	60	44	59	48	53	49	38	41	39	42	40	51
First-step Catalyst	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O	ATTM + H_2O
Temperature (°C) 1st	350	350	375	375	400	400	350	350	375	375	400	400
Second-step addition	None	None	None	None	None	None	None	None	None	None	None	None
Temperature (°C) 2nd	350	350	350	350	350	350	350	350	350	350	350	350
Hand Shaking	-	+	-	+	-	+	-	+	+	+	-	+
Shaking Times		over 300		over 300		over 300		over 300	under 100	over 300		over 300
Conversion (mol %)	45.0	64.4	26.4	66.7	56.6	66.0	46.0	82.7	73.9	89.4	50.0	76.9
Products (mol%)												
Tetralin	31.3	49.1	20.4	46.9	38.9	44.7	29.5	58.6	47.4	76.5	32.1	53.1
Naphthalene	45.8	67.5	23.1	72.6	59.8	72.6	37.4	79.5	79.1	86.2	50.5	75.9
5,6,7,8-Tetrahydro-2-naphthol	0.8	0.8		0.6	0.4	1.0	1.4	1.4	3.1	3.2	1.5	4.2
2-Naphthol	0.8	0.8	0.1	0.6	0.2	1.0	1.4	0.4	3.2		0.5	2.2
OctahydroDNE	0.4	0.3	0.2	0.3	0.3	0.4	0.2	0.8	0.5	0.8		0.7
TetrahydroDNE	5.3	5.1	4.3	6.1	6.6	6.0	7.2	12.0	6.9	5.7	7.7	8.5

Effect of H_2O/ DNE Ratio

In the test discussed above, the weight ratio of H_2O/DNE was maintained at 0.56 for the determination of role of water addition on hydrogenation of DNE. We have determine the optimum amount of added water. This was done by examining the relationship between the conversion of DNE and amount of added D_2O. Figure 2 shows the relationship between the amount of D_2O addition and the conversion of DNE from the runs at 350 °C for 30 min. Figures 3 and 4 also show the relationship between DNE conversion and weight ratio of D_2O/DNE and that of D_2O/ATTM, respectively. Because the trend of the change of DNE conversion on the amount of added D_2O is the same of those both on the weight ratio of D_2O/DNE and D_2O/ATTM, we will discuss on the relationship between DNE conversion and the amount of added D_2O. The conversions of DNE gradually increase from 46 % to 100% with increasing water amount from 0 to 0.2 g corresponding to a D_2O/DNE weight ratio of about 0.93, and they decrease from 100% to 60 % with further addition of water. These results also clearly indicate that 0.026 of the ratio of ATTM to D_2O is optimum for conversion of DNE under the conditions employed. It seems that since water is used for the preparation of effective catalyst from ATTM, the conversion of DNE is large up to 0.235 g of D_2O. However water itself has a negative effect for the hydrogenation of DNE, further additions of D_2O over 0.235 g seem to cause the decrease of the conversion of DNE.

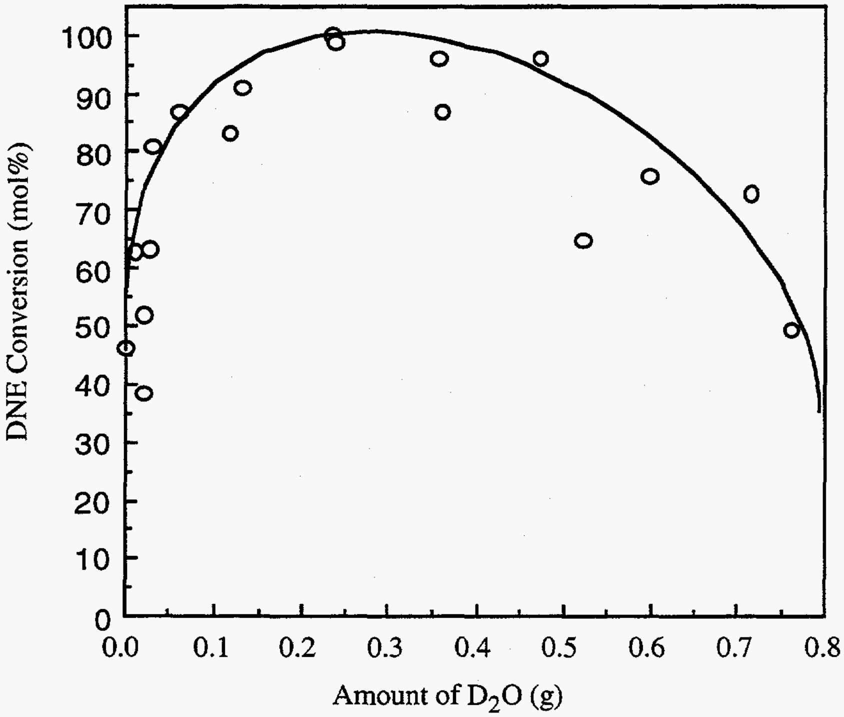

Fig. 2 Effect of addotion of D_2O on conversion of 2,2'-dinaphthyl ether (DNE) at 350 °C for 30 min. in 25 mL reactor. DNE: 0.216g; ATTM: 0.006g; n-C_{13}: 1.47g

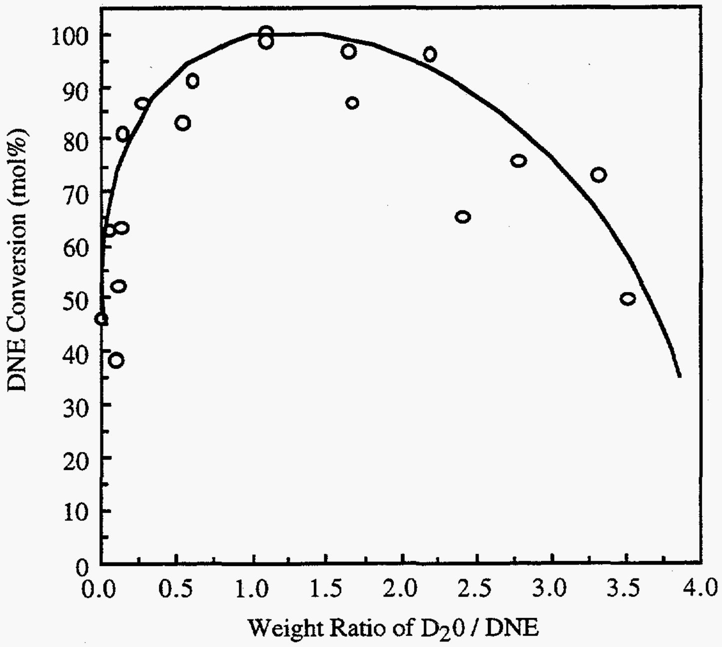

Fig. 3 Relationship between weight ratio of D_2O/DNE and DNE conversion at 350 °C for 30 min in 25 mL reactor. DNE: 0.216g; ATTM: 0.006g; n-C13: 1.47g

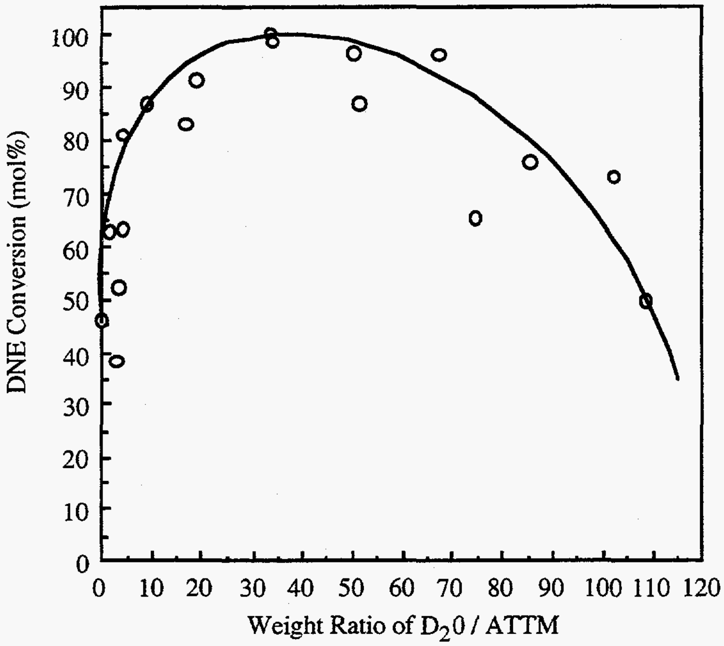

Fig. 4 Relationship between weight ratio of D_2O/ATTM and DNE conversion at 350 °C for 30 min in 25 mL reactor. DNE: 0.216g; ATTM: 0.006g; n-C13: 1.47g

CONCLUTIONS

A proper amount of added water has a strong promoting effect on hydrogenation and hydrogenolysis of DNE using molybdenum sulfide catalyst in-situ generated from ATTM. We have found that the addition of water is not effective for DNE conversion, but is effective for the preparation of active catalyst from ATTM for hydrogenation and hydrogenolysis of DNE.

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2. High Temperature Simulated Distillation GC and HDS Study on Catalytic Upgrading of Atmospheric and Vacuum Resids Using Dispersed and Supported Mo-Based Catalysts

INTRODUCTION

With an ultimate goal of exploring the potential of dispersed and supported catalysts for coal/resids coprocesssing process, we conducted a preliminary study on resid upgrading using both water-soluble and oil-soluble precursors of Mo sulfide catalysts as well as laboratory-prepared and commercial supported bimetallic catalysts. This report presents a summary on upgrading of two petroleum resids (atmospheric and vacuum resids) in terms of boiling point reduction and hydrodesufurization. High-temperature SimDis (HT-SimDis) GC analysis was adopted to evaluate the resids and their hydroprocessing products from laboratory batch reactors.

Research on resid upgrading as well as coal conversion aims at effective and efficient conversion and utilization of heavy hydrocarbon resources. With growing worldwide demand for petroleum products, much attention has been paid on upgrading petroleum resids to middle distillates (1). However it has been a challenge to process petroleum resids because of the large sizes and structural complexity of the resid molecules and their high boiling point range, and their high contents of sulfur, nitrogen and metals. At the same time, the average quality of crude is becoming worse because of a progressive decrease in API gravity (i.e., an increase in density) and a rise in sulfur content (2). As a consequence, there is a growing interest in converting heavy feed stocks (petroleum resids and heavy oils) into lower boiling products of high quality with low level of sulfur content. Worldwide, the sulfur contents of light oils will be limited to 500 ppm in EEC by 1996 and in Japan by 1997 (3). It is expected that further lower sulfur content and lower aromatics content of diesel fuel will be required by regulations in the near future (4). Therefore, desulfurization of feedstock to produce distillate fuels, particularly diesel fuels and gasoline, has become an important research subject.

Hydroprocessing is one of the important ways of petroleum resid upgrading. The main purpose of resid upgrading is to reduce the boiling point range as well as to remove sulfur, nitrogen and metals from resids. It is necessary to characterize resids and their products with various techniques that indicate their compositional features. Because petroleum resids are complex mixtures which contain hundreds of compounds with high molecular weights, characterizing resids is a tedious and complicated task. Laboratory-scale distillation tests are widely used for determining boiling point range of crude oil and their products (5). However, highly refined data by using this method would require tremendous amounts of time and labor. Furthermore, the boiling point range that can be determined by laboratory distillation operation is limited, particularly for resids.

Simulated distillation analysis by gas chromatography (SimDis GC) is an effective method which requires about one hour test. SimDis GC analysis achieved ASTM standard status in 1973 under the designation of D2887 and was revised three times in 1984,1989 and 1993. ASTM D5307 was defined in 1992 for determining the crude oil boiling point range . However, both of them can only be applied to fractions with final boiling point up to 1000°F/538°C (6,7). Consequently, there are various techniques being used in order to determine the boiling point distribution of heavy resids. Padlo et al. studied SimDis by HPLC equipment using an evaporative light scattering detector (8). Bacaud et al. performed modeling based on simulated distillation to evaluate the hydroprocessed resids (9). Klein and coworkers used SimDis results as part of analytical data for resid structure modeling (10). High-temperature simulated distillation analysis by GC (HT-SimDis) is a newly developed method for determining the boiling point range of heavy petroleum fraction up to 1400°F/760 °C and has not been widely applied to petroleum industry and research community.

In this report we present the preliminary results on our attempts to upgrade two types of petroleum resids, particularly with regard to the reduction of the molecular weight of the feed stock to material with boiling points (examed by HT-SimDis GC) below 540 °C and the removal of sulfur.

EXPERIMENTAL SECTION

Materials

Two resids, an atmospheric resid (AR) and a vacuum resid (VR2), were used in this study which were obtained from Marathon Oil Company. Four catalysts, a commercial Co-Mo/alumina (Shell 344TL), a laboratory-prepared mesoporous zeolite-supported Co-Mo/MCM-41, two dispersed molybdenum sulfide catalyst precursors including ammonium tetrathiomolybdate (ATTM) and molybdenum di(2-ethylhexyl)phosphoroidthioate (Molyvan L), were tested for hydroprocessing of both resids. Prior to the catalytic tests, Co-Mo/MCM-41 and Shell 344TL catalysts were sulfided in 100-mL autoclave using 6% CS_2 in n-dodecane under hydrogen pressure in a temperature-programmed manner: first at 250°C for 2 h and then at 300°C for 3 h. Detailed procedure for catalyst preparation and sulfidation is given elsewhere (11,12). After sulfidation, the catalysts were stored in n-tridecane before use. Our experience shows that such a procedure is effective for sulfidation in batch reactors (13). ATTM was obtained from Aldrich Chemical Company. Molyvan L, which is a stable organic liquid additive containing 8.1 wt% Mo in the form of molybdenum di(2-ethylhexyl)phosphoroidthioate, was provided by R.T. Vanderbilt Company, Norwalk, CT. The amounts of ATTM and Molyvan L loaded are reported in metal wt

% (not the compound itself) based on the weight of resid feed.

HT-SimDis GC Analysis

The gas chromatographic analysis was performed using Hewlett-Packard Model 5890 II Plus GC with a flame ionization detector and temperature programmable cool on-column injector. A 6 m x 0.53 mm high temperature megabore column (P/N SD-002HTC) from Separation System Inc. was used for HT-SimDis GC analysis. The injector temperature was always maintained 3 °C higher than column temperature. A Hewlett-Packard ChemStation software (B.02.04) was used for on-line data acquisition and SimDis Expert software (V 5.0) was used for post-run SimDis data analysis. Prior to the injection, the samples were diluted with carbon disulfide to about 2 wt%. The injection volume was 1.0 µL. The retention time standard containing normal hydrocarbons from C_5-C_{100} was used for HT-SimDis calibration. Another retention time standard used is a mixture called Polywax 655 containing C_5-C_{20} hydrocarbons and CS_2.

Estimation of Asphaltene Content

The contents of asphaltenes of the resids, which are defined as hexane-insoluble but toluene-soluble fraction, were estimated by their n-hexane and toluene solubilities. In order to do this estimation, 4 gram of AR or VR2 resid was dissolved in 400 mL hexane using ultrasonic bath for 1 hour and then filtered with 0.45 µm (pore size) membrane filter paper. The solid on filter paper was dried and weighed as hexane insoluble (HI) material. Similar procedure was used with toluene and estimated the toluene insolubles (TI). The amounts of asphaltenes in AR and VR2 were determined from the difference of hexane and toluene insolubles.

Hydroprocessing

The hydroprocessing was carried out at 350-450°C (with an interval of 25 °C) for 1 h in 25-mL horizontal micro autoclaves agitated vertically at 240 cycles/min. in a fluidized sand bath. In a typical run, 3 g resid, and 0.3 g catalyst were loaded into the reactor. The sealed reactor was flushed with H_2, pressurized to 1000 psig (6.9 MPa), and then plunged into the sand bath preheated to a given temperature. After the reaction, the reactor was quenched in cold water bath and then allowed to cool down to room temperature. After collecting a small part of the reaction products from well shaken reactor for sulfur analysis, the rest was recovered using CS_2 solvent followed by filtration.

The products were analyzed using HT-SimDis GC and the results are reported according to the cut point range classified in Table 5 which is similar to the classification proposed by Altgelt and Boduszynski (14). Resid conversion was calculated from the sum of >340 °C (boiling point) fractions and/or >540 °C fractions. The sulfur content was analyzed before and after the reaction using a SC-132 sulfur analyzer from LECO Corporation. Hydrodesulfurization (HDS) effect was evaluated by the sulfur conversion of resids.

Table 5. Boiling point range of different fractions.

Boiling point ranges °C	°F	Fraction
IBP-130	IBP-266	Light Naphtha
130-220	266-428	Heavy Naphtha
220-340	428-644	Atmospheric Gas Oil
340-450	644-842	Light Vacuum Gas Oil
450-540	842-1004	Heavy Vacuum Gas Oil
540-700	1004-1292	Super Heavy Gas Oil
>700	>1292	Nondistillable Residue

RESULTS AND DISCUSSION

Selection of HT-SimDis Conditions

High temperature SimDis (HT-SimDis) GC analysis of AR and VR2 resids was performed at different GC conditions. Table 6 gives the three GC methods with different GC analysis conditions. In the first method (TP1), detector temperature was kept low compared to the other two methods. Results showed that the detector at low temperature is not sensitive enough to detect the high molecular weight compounds. In third method (TP3), column temperature was raised at 15 °C/min. whereas in other two methods it was 10 °C/min.

Table 6. Different GC Methods for HT-SimDis GC Analysis

		Column Temperature Program					
Method	Detector Temp. (°C)	Initial Temp. (°C)	Initial Time (min.)	Rate (°C/min)	Final Temp. (°C)	Final Time (min.)	Total time (min.)
TP1	350	40	1	10	425	15.5	55
TP2	435	40	1	10	425	15.5	55
TP3	435	40	1	15	425	28.8	60

Analysis of both resids and their products demonstrated that among three methods (TP1, TP2 and TP3), TP2 is a good method with respect to detector sensitivity and elution of high molecular weight compounds. Hence all the subsequent analyses were done using TP2 method.

Table 7. HT-SimDis GC analysis of various pure organic compounds.

	True boiling point		HT-SimDis BP		Deviation	
Compounds	°C	°F	°C	°F	°C	°F
Cycloalkane:						
Methylcyclohexane	101	214	104.3	219.8	3.3	6.0
trans-1,3-Dimethylcyclohexane	124	255	132.6	270.8	8.6	15.6
Hexylcyclohexane	221	430	223.1	433.6	4.0	3.8
cis-Decalin	193	379	197.4	387.3	4.4	7.9
trans-Decalin	185	365	193.9	380.9	8.9	15.9
Ethylcyclohexane	130	266	127.6	261.7	-2.4	-4.3
Propylcyclohexene	155	311	155.9	312.6	0.9	1.6
Butylcyclohexane	180	356	178.9	353.9	-1.1	-2.1
Aromatics:						
Toluene	110	230	117.5	243.5	7.5	13.5
p-xylene	139	282	139.6	283.2	0.6	1.0
Ethylbenzene	136	277	142.7	288.9	6.7	12.1
Naphthalene	218	424	218.2	424.7	0.2	0.3
Cyclohexylbenzene	239	462	240.0	464.0	1.0	1.8
2-Methylnaphthalene	241	466	237.0	458.7	-4.0	-7.1
1-Methylnaphthalene	240	464	227.4	441.4	-12.6	-22.6
2,6-Dimethylnaphthalene	262	504	275.1	527.2	13.1	23.6
1,5-Dimethylnaphthalene	266	511	277.6	531.7	11.6	20.9
Fluorene	298	568	291.3	556.3	-6.7	-12.1
Biphenyl	255	491	258.1	496.5	3.1	5.5
p-Terphenyl	389	732	382.9	721.2	-6.1	-11.0
Phenanthrene	336	637	319.7	607.5	-16.3	-29.3
Anthracene	342	648	339.5	643.2	-2.5	-4.4
Pyrene	395	743	381.7	719.1	-13.3	-23.9
Chrysene	447	837	417.6	783.7	-29.4	-52.9
Heteroatom-containing compounds:						
Phenol	182	360	171.7	341.0	-10.3	-18.6
m-Cresol	203	397	196.5	385.8	-6.5	-11.6
2-Naphthol	285	545	284.1	543.4	-0.9	-1.6
Dibenzofuran	285	545	298.2	568.7	13.2	23.7
Quinoline	237	459	227.1	440.8	-9.9	-17.8
1.2.3.4-Tetrahydroquinoline	249	480	247.2	477.0	-1.8	-3.2
Acridine	346	655	348.6	659.4	2.6	4.6
Benzothiophene	221	430	219.2	426.5	-1.8	-3.3
Dibenzothiophene	332	630	317.1	602.8	-14.9	-26.8

In order to check the SimDis boiling point calibration especially for the mixtures containing various types of compounds, we also analyzed different types of compounds and estimated their boiling points using HT-SimDis method. In this case of pure compounds analysis the boiling points were taken from the initial boiling point of HT-SimDis boiling point distribution. Table 7 lists all the compounds, their estimated and true boiling points and the deviations of estimation. Results show that calibration is good for aliphatic hydrocarbons, however there is some deviation for aromatic compounds, oxygen, nitrogen and sulfur containing compounds especially with polycylic compounds.

Analysis of AR and VR2 Feed

Fig. 5 and Fig. 6 illustrate the HT-SimDis gas chromatograms of both AR and VR2 resids and their hexane soluble and hexane insoluble fractions. According to Table 5, contents of different fractions for both AR and VR2 resids are derived using HT-SimDis GC analysis and tabulated in Table 8. The amounts of asphaltenes for AR and VR2 feeds were estimated and the values are 9.22 and 14.02 wt%. Both AR and VR2 resids were found to be almost completely soluble in toluene, which indicated that essentially all hexane insolubles are asphaltenes in these resids. HT-SimDis gas chromatograms of AR and VR2 resids contain two major peaks. In the case of VR2 resid the second peak at high temperature region is more intense compared to that of AR resid indicating the higher content of high boiling fraction. HT-SimDis gas chromatograms of hexane insoluble (HI) fractions of both AR and VR2 resids show a single peak at high temperature. Comparison of these results show that hexane insoluble fractions contribute exclusively to the second peak of the chromatograms of the original resid. Fig. 5, Fig. 6 and Table 8 clearly show that VR2 feed contains more higher boiling fraction (>540 °C) and more asphaltenes compared to AR feed. The sulfur contents in AR and VR2 were 3.87 and 5.01 wt% respectively.

Table 8. HT-SimDis GC analysis and sulfur contents of AR and VR2 resids.

Sample	IBP-130	130-220	220-340	340-450	450-540	540-700	700-FBP	>340°C Sum	>540°C Sum	HI (wt %)	TI (wt %)	Asphaltene (wt %)	Sulfur (wt%)
AR feed	0.0	0.3	5.4	20.3	25.1	36.2	12.2	93.8	48.4	9.22	0.00	9.22	3.87
VR feed	0.0	1.0	2.9	4.7	12.6	59.7	18.1	95.1	77.8	14.14	0.12	14.02	5.01

Hydroprocessing of AR

Fig. 7 presents the fraction distribution of AR products from thermal runs at different temperature. It can be seen that, at ≤370°C, there is little change in fraction distribution. Above 375°C, the lighter fractions increase as the reaction temperature increase (as shown in four bars) and the heavier fractions (as shown in tree lines) decrease. It is considered that the heavy resid components were converted to light materials with lower molecular weight. There is little change in the contents of 450-540°C fraction from the runs at reaction temperatures of 350-400°C.

The earlier work in this laboratory has shown that there is a strong synergistic effect between ATTM and water in coal hydroliquefaction at relatively low temperatures (350-375°C). In order to find out whether this occurs with petroleum resids or not, we conducted several tests at the reaction temperatures of 350 and 375 °C. The data are listed in Table 9. The results show that for AR, ATTM did not improve the hydroprocessed products much, neither did adding water. This indicated that AR is more difficult to convert than low rank Wyodak coal at low temperature (350-375 °C). The sulfur contents in the table also show little difference between catalytic runs and thermal runs.

Table 9 The effect of ATTM and water on the resid processing

Expt. No	reaction Temp(°C)	ATTM (%)	water (%)	IBP- <130	130- 220	220- 340	340- 450	450- 540	540- 700	700- FBP	>340°C Conv.(%)	Sulfur (%)
25	350	No	No	0.0	0.1	3.5	20.2	24.9	38.5	12.4	-2.3	3.60
23	350	0.4	No	0.0	0.3	5.1	19.8	25.1	36.4	12.4	0.1	3.77
26	350	0.4	5.5	0.0	0.1	6.2	22.5	24.1	37.1	9.6	0.5	3.78
24	350	0.4	11	0.0	0.1	4.8	19.8	24.8	37.6	12.4	-0.9	3.43
1	375	No	No	0.0	0.3	5.2	20.6	25.8	35.7	11.9	-0.2	3.81
2	375	0.1	No	0.0	0.5	6.3	21.6	25.4	34.7	10.9	1.3	3.79
3	375	0.1	5.5	0.0	0.5	5.9	20.8	25.9	34.9	11.6	0.6	3.77
4	375	0.1	11.0	0.0	2.1	6.3	20.6	24.8	34.4	11.3	2.9	3.59
11	375	0.1	16.0	0.0	0.5	8.5	23.8	24.3	34.0	8.4	3.5	3.44
15	375	0.4	11.0	0.0	0.6	6.0	20.5	25.3	34.5	12.6	1.0	3.58
16	375	1.0	11.0	0.0	0.6	6.0	20.7	25.5	34.4	12.4	0.9	3.73
17	375	1.0	27.0	0.0	0.6	6.1	21.0	25.5	34.5	11.7	1.2	3.60

Note: wt% of water is based on the amount of resids.

Fig. 8 and Fig. 9 show the results of thermal run and ATTM run at different temperature. Compared with thermal run, adding ATTM achieved some improvement in >540 °C fraction conversion, but adding water over ATTM did not give any apparent improvement. For HDS, ATTM and water did not affect the results compared with thermal run.

Shell 344TL catalyst and MCM-41 supported Co-Mo catalyst were also tested to examine their effect on boiling point reduction and HDS. Both Shell 344TL and MCM 41 catalyst show little positive effect on AR heavy fraction conversion. Fig. 10 illustrates the effect of Shell 344TL on HDS conversion. It can be clearly seen that HDS improves significantly as reaction temperature increases, in the runs with Shell catalyst, but HDS shows only a little change with reaction temperature in the thermal runs. Moreover, increasing the amount of the Shell catalyst from 0.1 to 0.3 g definitely improved HDS at both 400 and 425°C. MCM-41 supported catalyst was not as effective as Shell 344TL in HDS but much better than noncatalytic run.

A complete summary of data for AR upgrading is given in Table 10.

Table 10 SimDis and Sulfur Analysis Data for Upgrading of AR (Marathon AR)

Expt.ID	Temp (C)	Catalyst		SimDist GC Analysis (%)													
			GC ID	IBP-<130	130-220	220-340	340-450	450-540	540-700	700-FBP	Frac. Sum	>340 Sum	>340°C Conv.(%)	>540 Sum	>540°C Conv. (%)	Sulfur (%)	Sulfur Conv. (%)
AR Feed	-	-	arfeed2	0.0	0.3	5.4	20.3	25.1	36.2	12.2	99.5	93.8		48.4		3.87	
AR-HS	-	-	AR-HSM	0.0	0.4	7.3	23.3	24.9	34.4	9.2	99.5	91.8		43.6			
AR-HI	-	-	AR-HIM	0.0	1.2	3.4	4.0	5.5	44.7	40.7	99.5	94.9		85.4			
BW1	375	No	bw1a	0.0	0.3	5.2	20.6	25.8	35.7	11.9	99.5	94.0	-0.2	47.6	1.7	3.81	1.6
BW2	375	0.1%ATTM	bw2a	0.0	0.5	6.3	21.6	25.4	34.7	10.9	99.4	92.6	1.3	45.6	5.8	3.79	2.0
BW3	375	0.1%ATTM/5.5%H2O	bw3a	0.0	0.5	5.9	20.8	25.9	34.9	11.6	99.6	93.2	0.6	46.5	3.9	3.77	2.7
BW4	375	0.1%ATTM/11%H2O	bw4	0.0	2.1	6.3	20.6	24.8	34.4	11.3	99.5	91.1	2.9	45.7	5.6	3.59	7.2
BW11	375	0.1%ATTM/16%H2O	bw11	0.0	0.5	8.5	23.8	24.3	34.0	8.4	99.5	90.5	3.5	42.4	12.4	3.44	11.1
BW15	375	0.4%ATTM/11%H2O	bw15	0.0	0.6	6.0	20.5	25.3	34.5	12.6	99.5	92.9	1.0	47.1	2.7	3.58	7.5
BW16	375	1.0%ATTM/11%H2O	bw16	0.0	0.6	6.0	20.7	25.5	34.4	12.4	99.6	93.0	0.9	46.8	3.3	3.73	3.7
BW17	375	1.0%ATTM/27%H2O	bw17	0.0	0.6	6.1	21.0	25.5	34.5	11.7	99.4	92.7	1.2	46.2	4.5	3.60	6.9
BW27	375	0.3g Co-Mo 344S	BW27	0.0	1.0	9.0	23.2	23.5	33.8	9.0	99.5	89.5	4.6	42.8	11.6	2.78	28.2
BW5	400	No	bw5	0.0	2.7	10.6	23.7	23.8	29.0	9.6	99.4	86.1	8.2	38.6	20.2	3.68	4.8
BW6	400	0.1%ATTM	bw6	0.0	2.1	10.8	24.3	25.1	29.5	7.6	99.4	86.5	7.8	37.1	23.3	3.62	6.4
BW12	400	0.1%ATTM/5.5%H2O	bw12	0.0	0.7	10.4	23.7	24.6	30.6	9.4	99.4	88.3	5.9	40.0	17.4	3.50	9.5
BW18	400	0.1g Co-Mo 344S	bw18	0.0	1.4	9.3	23.1	25.8	30.6	9.3	99.5	88.8	5.3	39.9	17.6	2.49	35.5
BW19	400	0.2g Co-Mo 344S	bw19	0.0	0.9	7.6	23.0	25.8	31.7	10.4	99.4	90.9	3.1	42.1	13.0	2.32	40.2
BW20	400	0.3g Co-Mo 344S	bw20	0.0	1.8	11.7	29.5	29.0	24.6	2.8	99.4	85.9	8.4	27.4	43.4	2.24	42.0
BW7	425	No	#7	0.8	7.9	19.8	27.1	19.6	21.0	2.9	99.1	70.6	24.7	23.9	50.6	3.22	16.8
BW8	425	0.1%ATTM	bw8	0.7	9.2	21.7	28.2	19.0	17.0	3.2	99.0	67.4	28.1	20.2	58.3	3.19	17.6
BW13	425	0.1%ATTM/5.5%H2O	bw13	0.2	5.9	19.4	27.0	19.9	20.1	6.5	99.0	73.5	21.6	26.6	45.0	3.24	16.3
BW21	425	0.3g Co-Mo 344S	#21	0.6	7.1	18.0	26.7	21.2	22.4	3.2	99.2	73.5	21.6	25.6	47.1	1.24	68.0
BW22	425	0.1g Co-Mo 344S	bw22	0.4	4.1	15.1	26.2	23.0	24.0	6.1	98.9	79.3	15.5	30.1	37.8	2.06	46.8
BW29	425	0.3g MCM-41	#29	0.4	6.2	16.8	26.0	21.7	25.2	2.8	99.1	75.7	19.3	28.0	42.1	2.07	46.5
BW9	450	No	bw9a	1.0	17.8	23.0	22.1	14.2	16.1	4.9	99.1	57.3	38.9	21.0	56.6	2.70	30.2
BW10	450	0.1%ATTM	bw10	0.0	14.7	34.9	23.6	11.8	12.5	2.1	99.6	50.0	46.7	14.6	69.8	2.73	29.5
BW14	450	0.1%ATTM/5.5%H2O	bw-14a	3.7	21.6	27.9	21.2	11.0	12.2	1.7	99.3	46.1	50.9	13.9	71.3	2.71	30.0
BW25	350	No	bw25	0.0	0.1	3.5	20.2	24.9	38.5	12.4	99.6	96.0	-2.3	50.9	-5.2	3.60	7.0
BW23	350	0.4%ATTM	bw23	0.0	0.3	5.1	19.8	25.1	36.4	12.4	99.1	93.7	0.1	48.8	-0.8	3.77	2.5
BW26	350	0.4%ATTM5.5%H2O	bw26	0.0	0.1	6.2	22.5	24.1	37.1	9.6	99.6	93.3	0.5	46.7	3.5	3.78	2.4
BW24	350	0.4%ATTM11%H2O	bw24	0.0	0.1	4.8	19.8	24.8	37.6	12.4	99.5	94.6	-0.9	50.0	-3.3	3.43	11.4
BW28	350	0.3g Co-Mo 344S	bw28	0.0	0.9	8.6	20.0	20.3	40.0	9.8	99.6	90.1	3.9	49.8	-2.9	3.16	18.3

AR asphaltene content = 9.22 wt%.

Hydroprocessing of VR2

Fig. 11 illustrates the distribution of products from thermal runs of VR2 at different temperatures. Like the case for AR, the lighter fractions (< 450 °C) increase and the heavier fractions (> 540 °C) decrease as the reaction temperature increases. This indicates that reaction temperature is one of the most important factors in resid hydroprocessing.

Fig. 12 shows the effect of temperature on distribution of different fractions of hydroprocessed products from VR2 over Shell 344TL catalyst. Results show that there is a significant influence of temperature on product distribution. It can be clearly seen that, with increasing reaction temperature, lighter fractions (below 450 °C) increase and heavier fractions (above 540 °C) decrease, which indicated that conversion of >540 °C fraction is higher at higher temperatures leading to more lighter fractions.

Fig. 13 shows the conversion of >540 °C fraction in VR2 in thermal and catalytic runs at different temperatures. Generally, there is not much difference among different catalysts in terms of reducing boiling point range of VR2 compared with thermal runs, although ATTM did show some favorable effect. At reaction temperature of 450 °C, it seemed that all catalysts act positively.

Fig. 14 shows the effect of adding water to ATTM catalytic runs. In the case of using 1 wt% ATTM, adding water slightly improved the resid conversion. However, there is only a small difference between the runs with and without water. We also conducted a few tests under other conditions but no greatly promising trend was found with ATTM plus water. It is known that the petroleum resid molecular structure is completely different from that of low rank coals although both contain hetero-polyaromatic molecules. Probably ATTM is not an effective catalyst precursor for resids upgrading under the conditions used.

Fig. 15 presents the VR2 HDS conversion over different catalysts at different temperature. The HDS results indicate that Shell 344TL is the best among all the catalysts tested in this study. MCM-41 supported catalyst also shows certain advantage in HDS of VR2 resid but not as good as expected from the model compound study (16). ATTM is not helpful to reducing sulfur content in resid hydroprocessing. The use of Molyvan L only show a little benefit in HDS.

A complete summary of data for VR2 upgrading is given in Table 11. The data for SimDis analysis and sulfur analysis of the upgrading products from hexane-soluble fraction of VR2 are summarized in Table 12. Also included in Table 12 are the data for the products from upgrading of VR2 in the presence of hexane solvent (where 2:1 means 6 g hexane:3 g resid, and 1:1 means 3 g hexane: 3 g resid) during the reaction.

Table 11 SimDis and Sulfur Analysis Data for Upgrading of Vacuum Resid (Marathon VR2)

Expe. No.	Catalyst w/o	Catalyst Amount	Temp. (°C)	Added H2O(%)	Recovery Solvent	IBP- <130	130- 220	220- 340	340- 450	450- 540	540- 700	700- FBP	Frac. sum	>540 Sum	>540°C Conv. (%)	Sulfur (wt%)	Sulfur Conv. (%)
VR2	__	__	__	__	__	0.0	1.0	2.9	4.7	12.6	59.7	18.1	99.0	77.8		5.01	
VR2-HS	__	__	__	__	__	0.0	0.3	0.5	1.6	12.9	63.7	20.4	99.4	84.1			
VR2-HI	__	__	__	__	__	0.0	1.5	3.7	3.5	3.4	43.9	43.6	99.6	87.5			
65	Thermal	__	375	No	Solvent	0.0	0.6	1.6	4.1	13.9	60.4	18.4	99.0	78.8	-1.3	4.62	7.8
40	Thermal	__	400	No	No Solvent	0.2	1.7	7.3	9.7	14.7	52.4	13.0	99.0	65.4	15.9	4.58	8.6
31	Thermal	__	425	No	No Solvent	3.2	10.2	18.1	18.7	17.6	27.7	3.7	99.2	31.4	59.6	4.53	9.6
31r	Thermal	__	425	No	Solvent	0.7	5.5	18.2	19.2	18.7	29.7	7.2	99.2	36.9	52.6	4.35	13.2
37	Thermal	__	450	No	No Solvent	3.3	14.8	26.4	19.5	13.4	18.9	2.8	99.1	21.7	72.1	2.92	41.7
37r	Thermal	__	450	No	Solvent	0.1	2.3	26.5	22.9	16.9	26.5	3.8	99.0	30.3	61.1	3.99	20.4
48	MCM(1)	0.3 g	400	No	Solvent	0.5	1.6	5.8	8.8	16.3	51.5	14.6	99.1	66.1	15.0	3.66	26.9
49	MCM(1)	0.3 g	425	No	No Solvent	2.6	8.9	16.1	18.4	19.3	29.8	4.0	99.1	33.8	56.6	3.79	24.4
51	MCM(1)	0.3 g	450	No	Solvent	0.0	10.6	25.6	20.9	15.6	23.4	3.2	99.3	26.6	65.8	2.17	56.7
50	MCM(1)	0.1 g	425	No	No Solvent	0.8	5.6	11.9	15.7	19.8	37.5	7.8	99.1	45.3	41.8	3.63	27.5
52	MCM(1)	0.1 g	450	No	Solvent	1.7	10.5	20.7	18.8	15.4	26.5	5.6	99.2	32.1	58.7	3.05	39.1
47	Shell	0.3 g	350	No	Solvent	0.0	1.9	4.5	5.4	12.3	54.9	20.0	99.0	74.9	3.7	4.51	10.0
46	Shell	0.3 g	375	No	Solvent	0.1	1.8	5.3	6.2	13.4	53.3	19.0	99.1	72.3	7.1	3.73	25.5
42	Shell	0.3 g	400	No	No Solvent	0.9	3.5	6.6	9.0	15.8	48.8	14.3	98.9	63.1	18.9	3.66	26.9
33	Shell	0.3 g	425	No	No Solvent	2.2	6.8	13.9	17.2	20.1	34.7	4.4	99.3	39.1	49.7	2.24	55.3
38r	Shell	0.3 g	450	No	Solvent	0.2	5.5	22.9	21.8	18.3	26.8	3.6	99.1	30.4	60.9	1.29	74.3
38	Shell	0.3 g	450	No	No Solvent	2.4	17.9	27.4	22.1	14.7	13.6	1.0	99.1	14.6	81.2	1.61	67.9
45	Shell	0.1 g	425	No	No Solvent	1.0	6.4	13.8	16.8	19.3	34.6	7.2	99.1	41.8	46.3	3.64	27.3
41	ATTM	0.032 g	400	No	No Solvent	0.8	4.4	8.9	11.4	16.7	45.6	11.3	99.1	56.9	26.9	4.47	10.8
32	ATTM	0.032 g	425	No	No Solvent	1.8	7.9	17.4	18.7	18.2	29.6	5.6	99.2	35.2	54.8	4.71	6.0
60	ATTM	0.032 g	425	11	No Solvent	2.0	5.5	12.7	16.5	19.8	35.5	7.1	99.1	42.6	45.2	4.07	18.7
39r	ATTM	0.032 g	450	No	Solvent	1.1	17.9	35.1	18.7	11.5	13.2	1.6	99.1	14.8	81.0	3.32	33.7
39	ATTM	0.032 g	450	No	No Solvent	6.5	18.0	26.3	18.6	12.2	15.5	2.2	99.3	17.7	77.2	2.88	42.5
34	ATTM	0.082 g	425	No	No Solvent	1.6	7.5	15.5	17.5	18.6	31.8	6.7	99.2	38.5	50.5	4.71	6.0
35	ATTM	0.082 g	425	5.5	No Solvent	2.4	7.4	14.9	17.7	19.1	32.2	5.4	99.1	37.6	51.7	4.64	7.4
36	ATTM	0.082 g	425	11	No Solvent	2.2	7.8	15.4	18.0	19.1	31.4	5.3	99.2	36.7	52.8	4.63	7.6
66	ATTM	0.032 g	375	No	Solvent	0.0	0.3	1.9	4.7	14.2	59.7	18.3	99.1	78.0	-0.3	4.87	2.8
67	ATTM	0.082 g	375	No	Solvent	0.0	0.6	2.4	5.8	15.1	58.4	17.3	99.6	75.7	2.7	4.50	10.2
68	ATTM	0.082 g	375	50	Solvent	0.0	0.5	3.0	3.9	13.4	59.0	19.4	99.2	78.4	-0.8	4.58	8.6
53	Shell(1)	1.0 g	425	No	No Solvent	1.2	7.2	14.8	18.2	20.6	31.5	5.6	99.1	37.1	52.3	3.45	31.1
53r	Shell(2)	1.0 g	426	No	No Solvent	1.6	7.4	14.4	18.7	21.1	30.3	5.5	99.0	35.8	54.0	3.72	25.7
70	MCM(3)	0.3 g	425	No	No Solvent	0.1	3.0	12.4	16.6	21.2	38.8	6.9	99.0	45.7	41.3	3.83	23.6
56(50r)	MCM(2)	0.1 g	425	No	No Solvent	1.0	5.6	11.7	15.6	20.1	37.6	7.6	99.2	45.2	41.9	3.87	22.8
57(49r)	MCM(2)	0.3 g	425	No	No Solvent	1.0	5.9	11.0	14.9	19.9	38.6	7.8	99.1	46.4	40.4	3.8	24.2
58	MCM(2)	1.0 g	425	No	No Solvent	1.1	5.7	12.4	15.9	19.9	36.5	7.5	99.0	44.0	43.4	4.4	12.2
64	MCM(2)	0.3 g	425	No	No Solvent	3.1	17.2	24.6	20.8	14.9	16.9	1.8	99.3	18.7	76.0	1.58	68.5
69	Molyvan	1.0%	375	No	Solvent	0.0	2.5	1.6	5.9	13.3	56.6	19.5	99.4	76.1	2.2	4.58	8.6
61	Molyvan	1.0%	425	No	No Solvent	3.1	4.7	11.2	15.3	19.3	38.6	7.0	99.2	45.6	41.4	3.89	22.4
62	Molyvan	0.4%	425	No	No Solvent	1.1	3.1	10.5	14.6	19.8	41.6	8.6	99.3	50.2	35.5	3.76	25.0
63	Molyvan	1.0%	450	No	No Solvent	7.7	25.0	26.4	16.3	10.3	12.5	1.2	99.4	13.7	82.4	2.82	43.7

Note: (1) and (2) represent first and second batch MCM or Shell sulfided.

Note A) Asphaltene content of VR2 = 14.02 wt%, and the content of toluene insolubles is 0.12 wt%.

Note B) MCM refers to MCM-41 supported sulfided Co-Mo catalyst, and Shell refers to the sulfided Shell 344 Co-Mo/Al203 catalyst.

Table 12 SimDis and Sulfur Analysis Data for Upgrading Products from Reactions of VR2 plus Hexane and VR2 Hexane-Soluble Fractions

Expt. No.	Catalyst (%)	added H2O(%)	Temp. (°C)	Reaction solvent	IBP-130	130-220	220-340	340-450	450-540	540-700	700-FBP	Frac. Sum	>540 Sum	>540 Conv.	Sulfur (%)	Sulfur Conv.
Reactions of VR2 + Hexane																
VR2	hexane:VR2=1:1 (Feed of 55 and 59)				0.0	1.5	2.6	4.1	11.8	54.9	24.3	99.2	79.2			
VR2	hexane:VR2=2:1 (Feed of 54)				0.3	3.7	0.9	2.7	10.9	58.3	22.3	99.1	80.6			
54	Shell 0.3 g		425	hexane:VR2=2:1	0.1	11.1	16.7	19.3	20.2	27.6	4.1	99.1	31.7	60.0	1.05	79.0
55	Shell 0.3 g		425	hexane:VR2=1:1	0.8	7.3	13.5	17.5	20.6	33.4	6.0	99.1	39.4	50.3	1.97	60.7
59	MCM 0.3 g		425	hexane:VR2=1:1	0.4	6.3	12.4	16.2	19.9	36.2	7.6	99.0	43.8	44.7	1.86	62.9
Reactions of VR2 Hexane solubles																
VR2-HS	Feed				1.3	6.0	0.5	0.9	10.9	61.5	18.1	99.2	79.6		4.17	
VR2-HI					0.0	3.9	8.3	8.3	7.6	24.9	46.3	99.3	71.2		6.90	
71	MCM 0.3 g		425		0.3	6.8	13.3	18.0	20.7	34.2	5.9	99.2	40.1	49.6	2.09	50.0
72	Shell 0.3 g		425		1.1	6.7	12.3	18.0	21.0	33.8	6.3	99.2	40.1	49.6	1.52	63.4
Resid loading for the reactions below was 0.5 grams																
		H2O Added (%)														
77	No catalyst		425		0.1	6.3	16.1	20.6	20.1	30.1	5.8	99.1	35.9	54.9		
78	ATTM 1.0%		425		0.3	6.4	13.3	17.4	20.6	35.6	5.6	99.2	41.2	48.2		
73*	ATTM 1.0%	No	425		0.0	6.2	15.1	19.2	20.5	32.4	5.7	99.1	38.1	52.1		
75	ATTM 1.0%	5.5	425		0.5	6.0	12.0	17.6	20.8	36.1	6.2	99.2	42.3	46.9		
76	ATTM 1.0%	11	425		0.6	5.2	10.0	13.9	19.9	42.2	7.3	99.1	49.5	37.8		
74	ATTM 1.0%	56	425		0.3	5.4	9.5	14.6	20.3	41.6	7.4	99.1	49.0	38.4		
79#	ATTM 1.0%	50	425	Two steps	0.0	3.4	9.1	15.2	21.1	43.6	7.2	99.6	50.8	36.2		

*Finely grounded ATTM powder was added to the reactor comparaed to normal ATTM. #The first step temperature for catalytic preparation was 375 °C and the second step reaction temperature was 425 °C with water removal prior to loading resid.

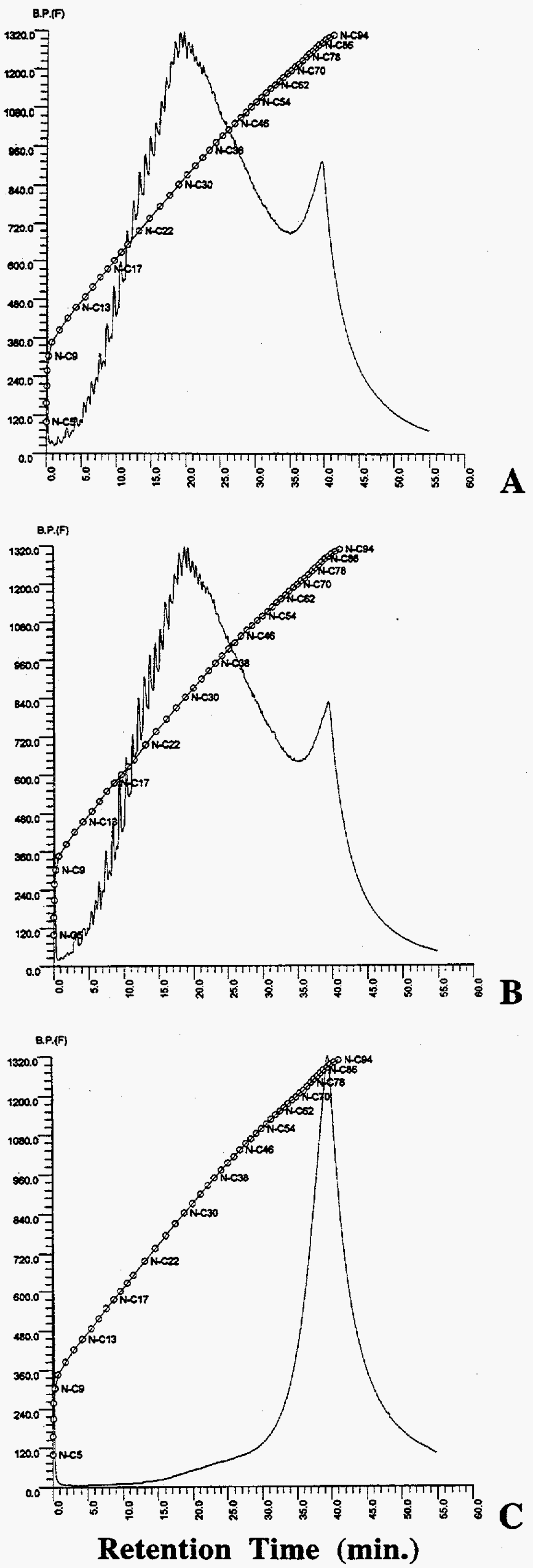

Fig. 5. HT-SimDis Gas Chromatograms of AR (A), AR-HS (B), and AR-HI (C)

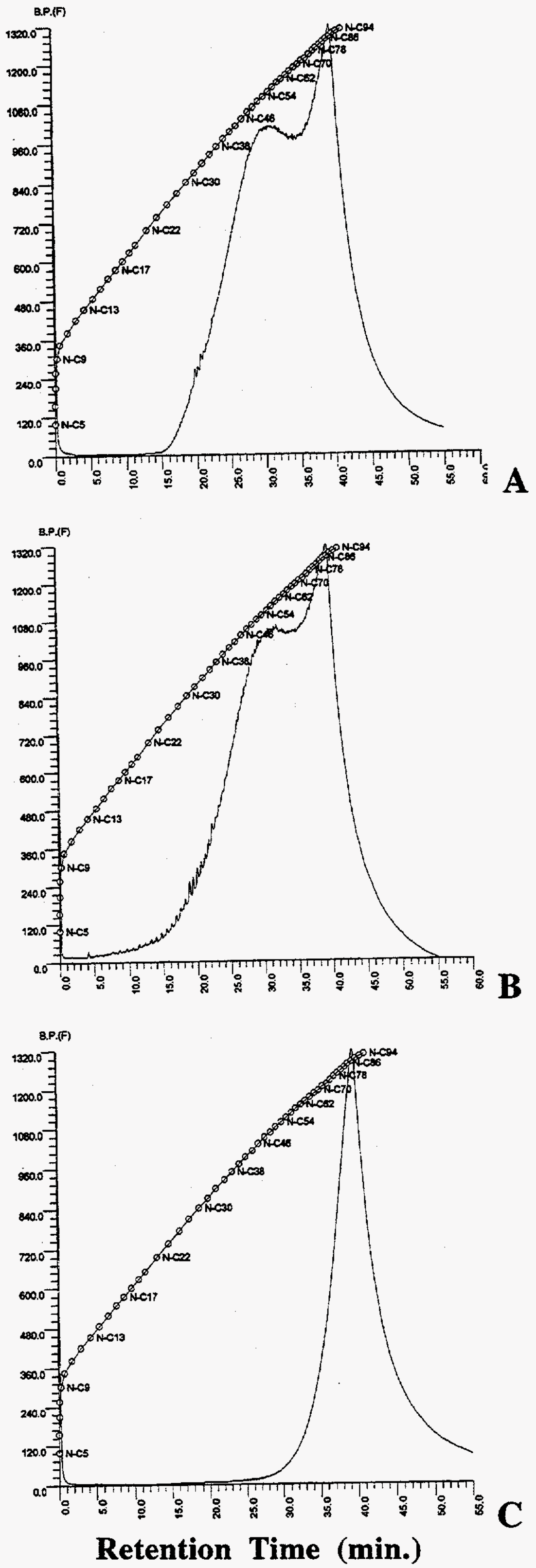

Fig. 6. HT-SimDis Gas Chromatograms of VR (A), VR-HS (B), and VR-HI (C)

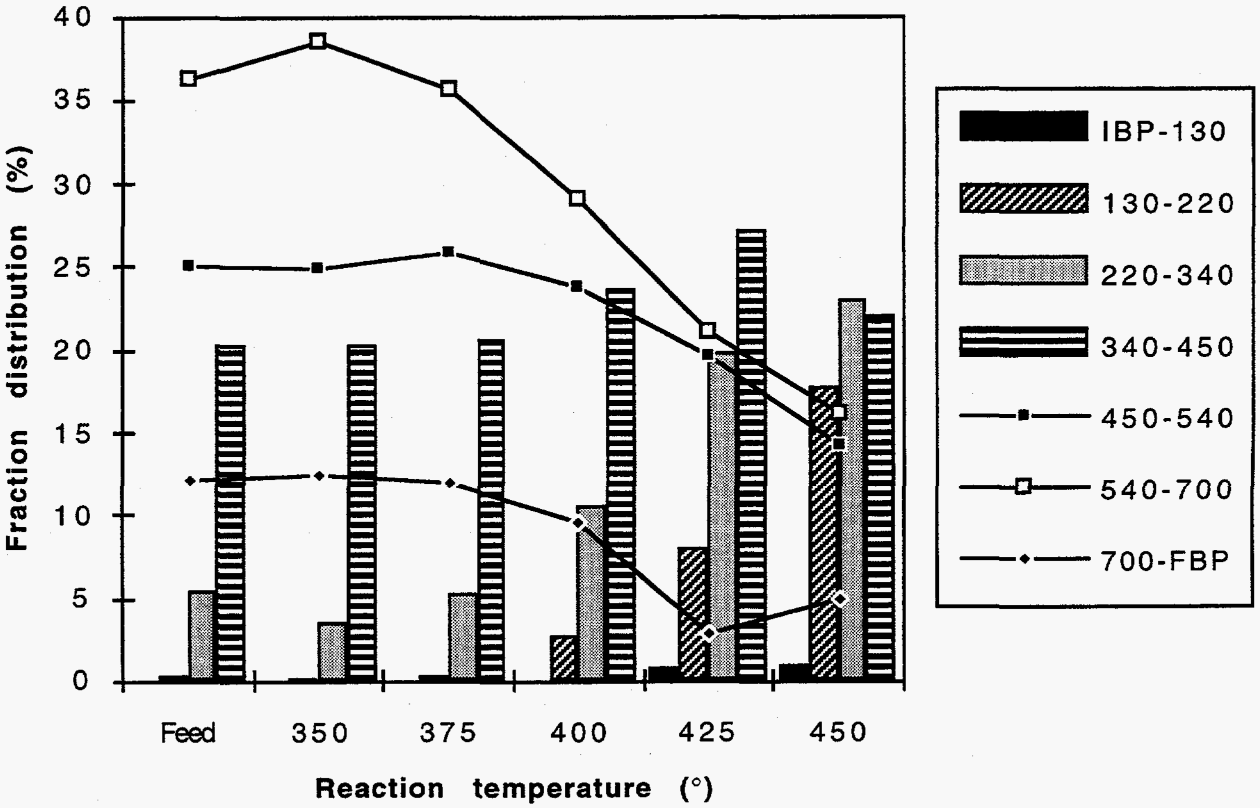

Fig. 7 AR products of thermal run at different temperature

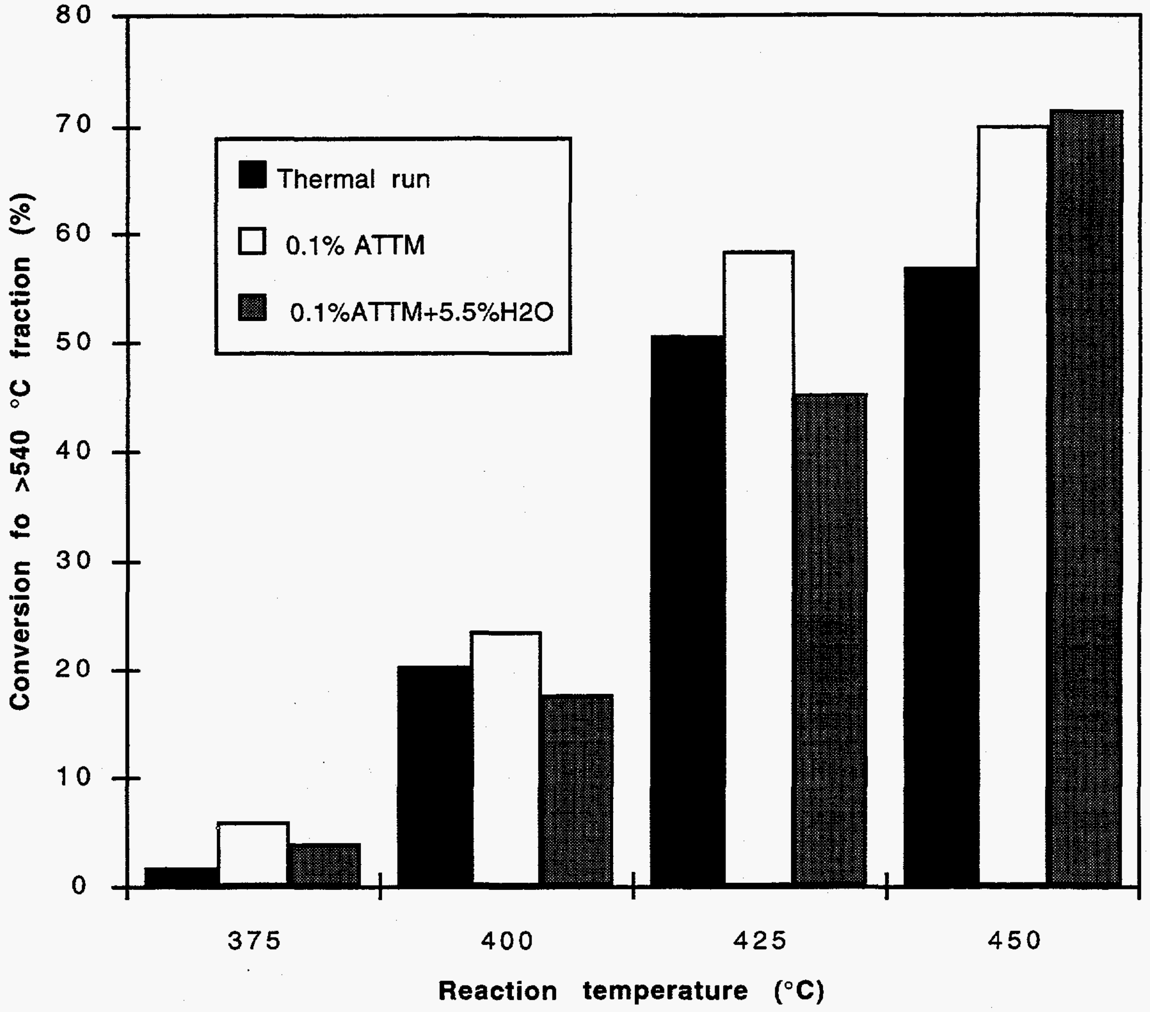

Fig. 8 AR product from catalytic run over ATTM and water

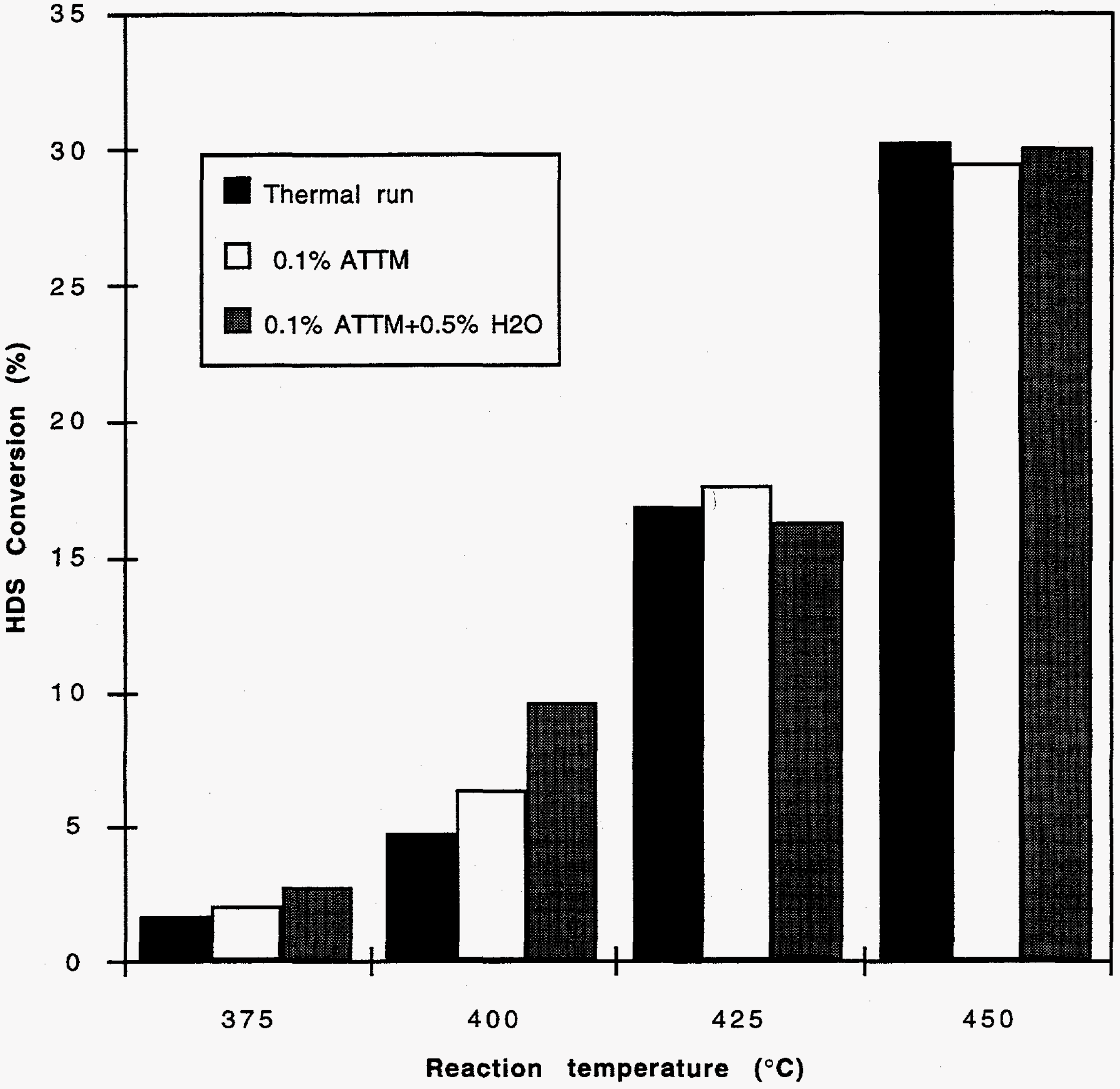

Fig. 9 HDS effect of catalytic run over ATTM and water

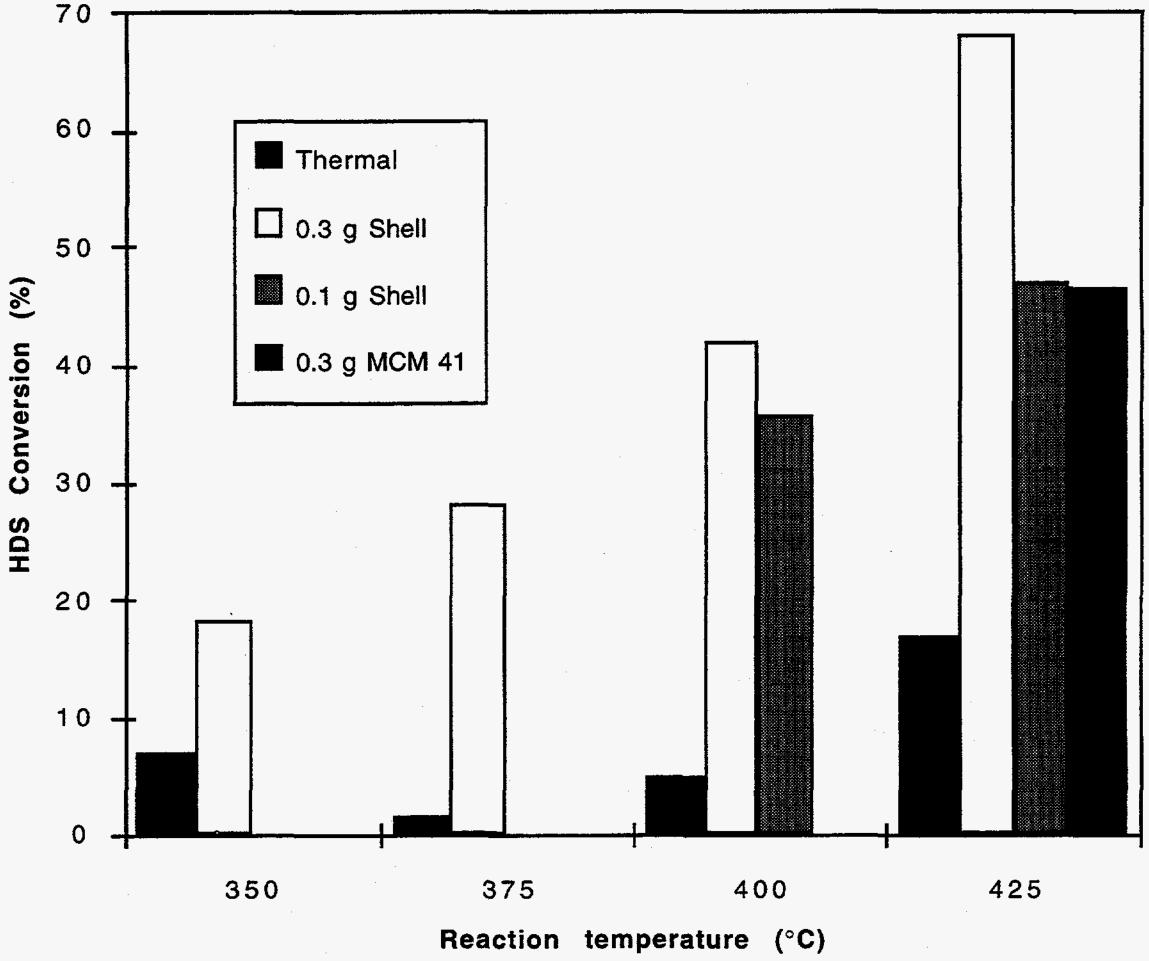

Fig. 10 HDS of AR thermal run and catalytic run over Shell 344TL at different temperatures

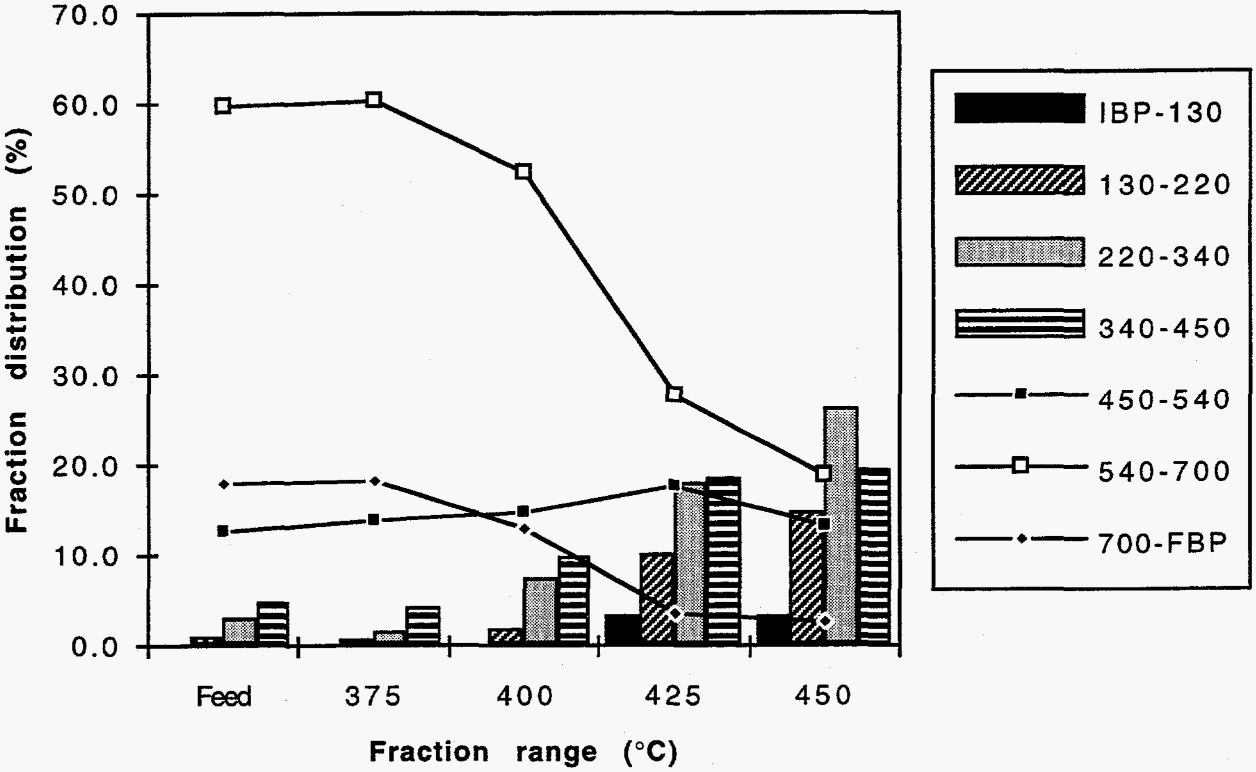

Fig. 11 Fraction distribution of VR2 thermal run at different temperatures

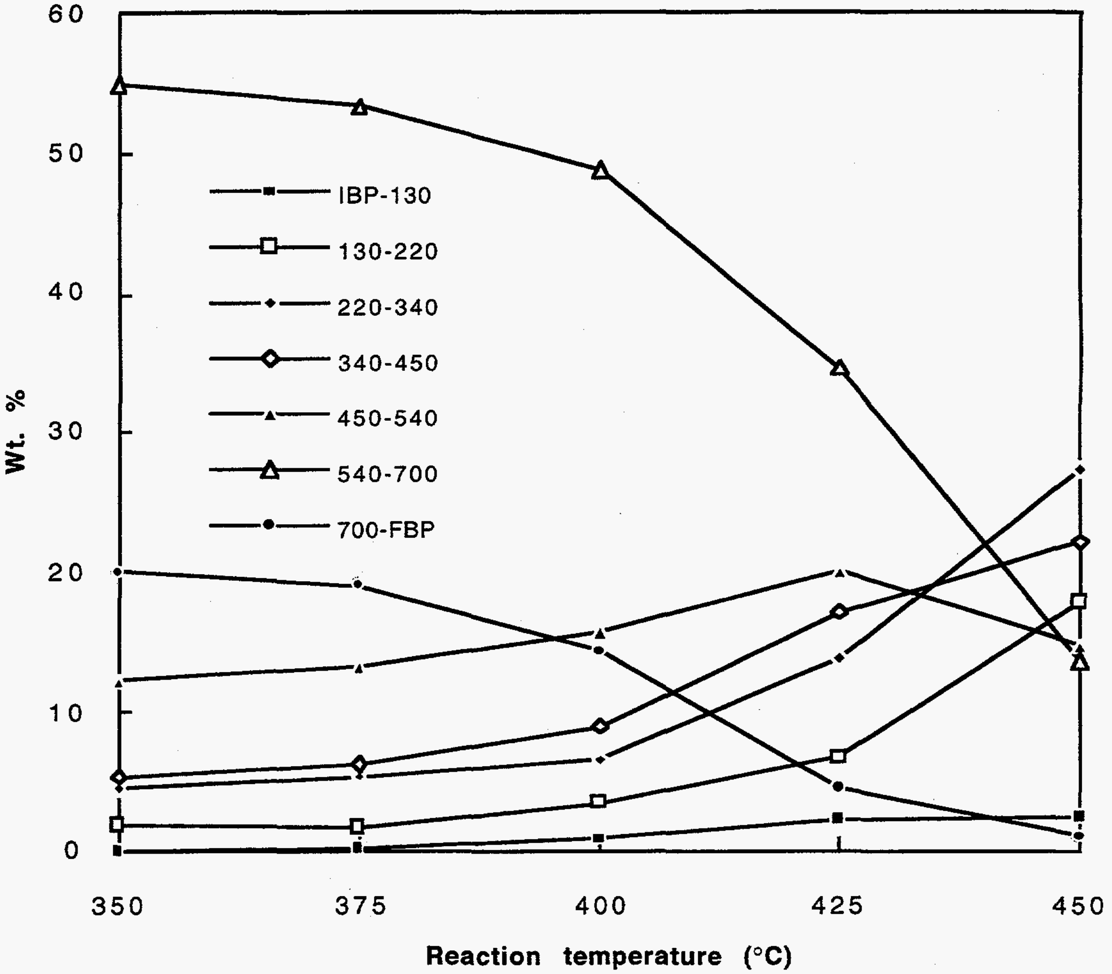

Fig. 12 Effect of temperature on yield of different fractions of VR2 resid hydroprocessing products over Shell 344TL catalyst (catalyst loading: 0.3 gram).

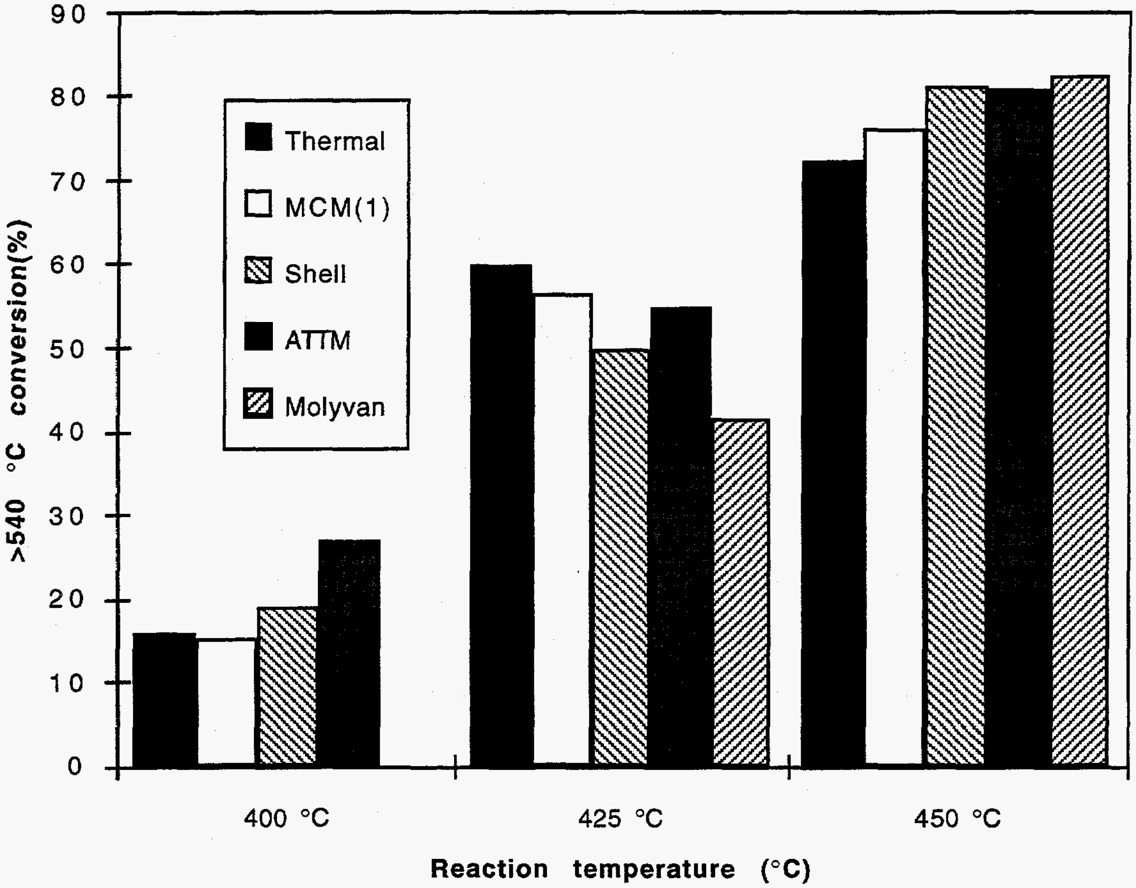

Fig. 13 Effect of differnet catalysts on yield of >540°C fraction conversion at different reaction temperatures

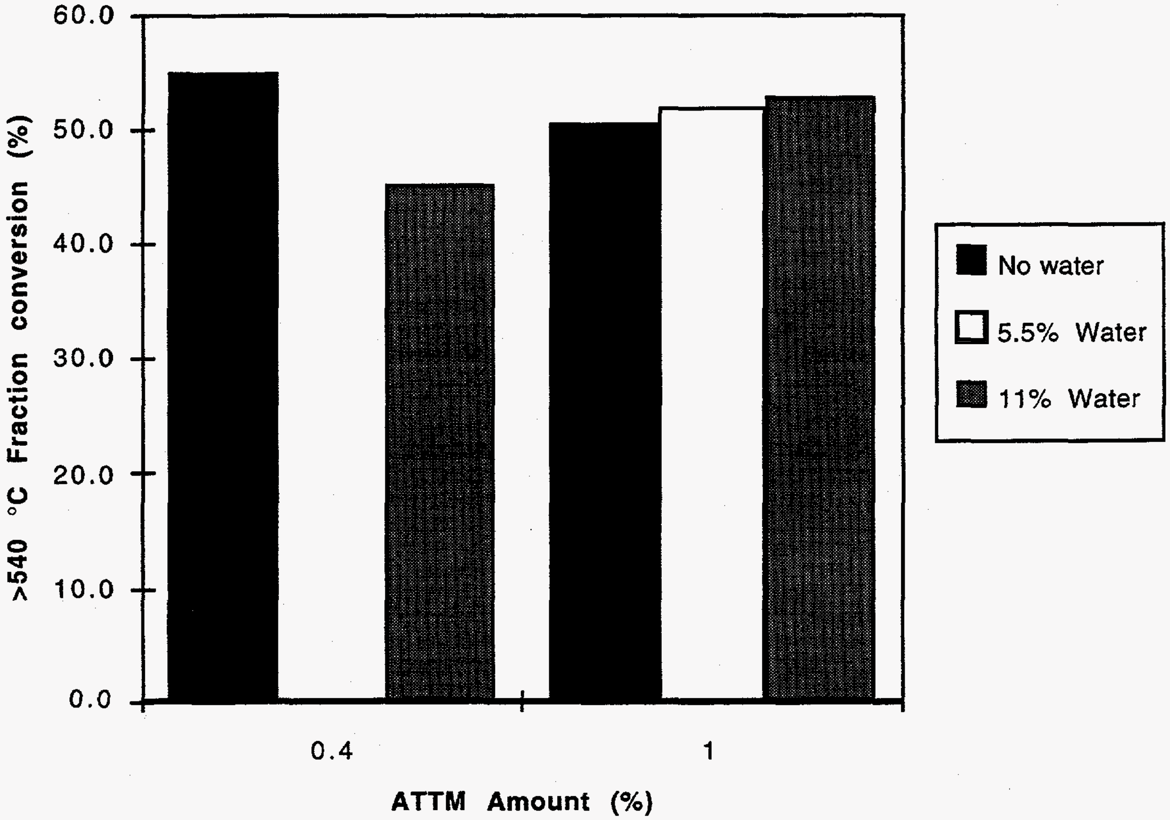

Fig. 14 Water effect on >540 °C fraction conversion over ATTM catalytic runs

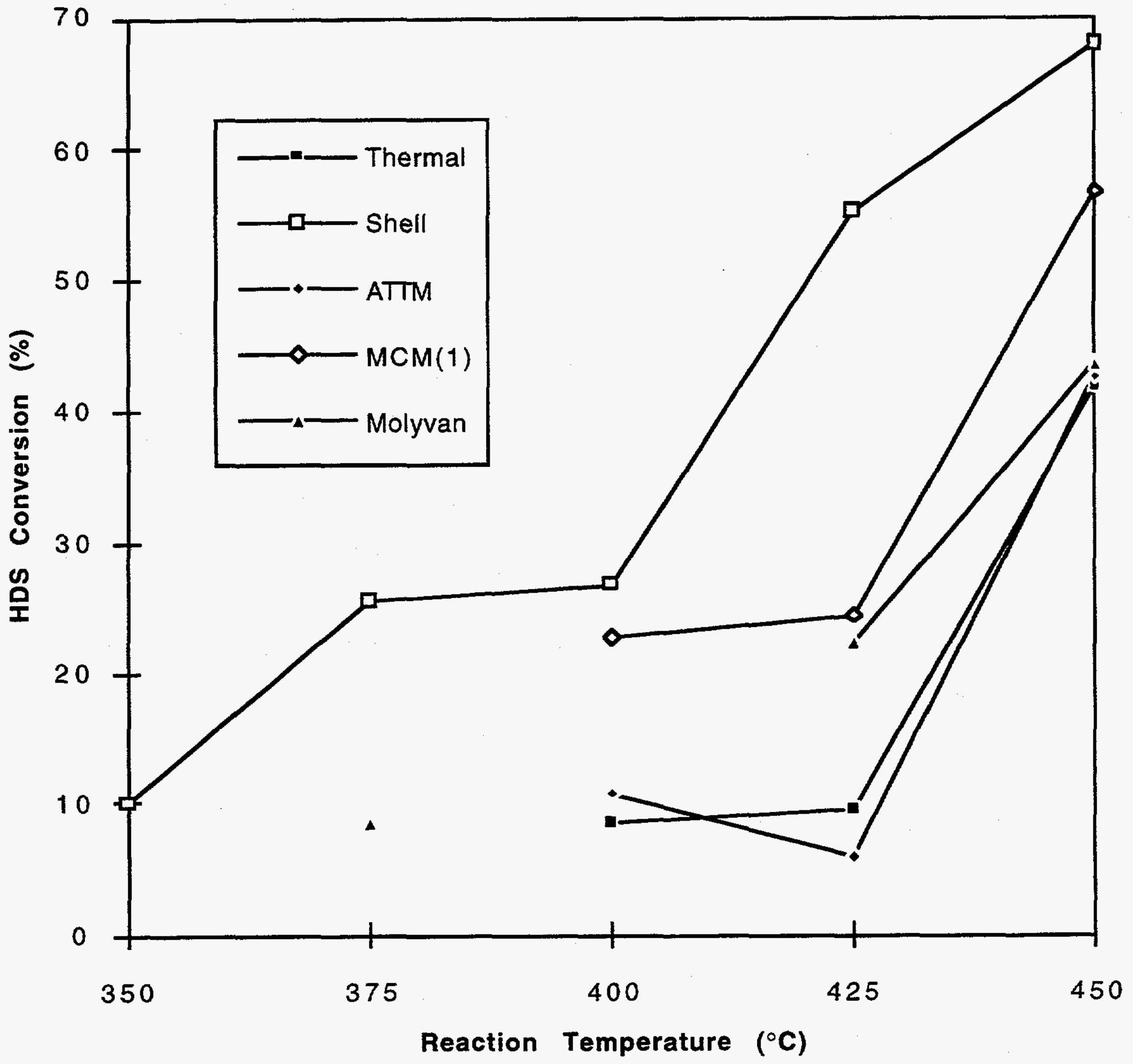

Fig. 15 HDS of VR2 thermal and catalytic runs at different temperatures

Conclusions

We have examined the effect of in-situ generated dispersed molybdenum catalyst and supported catalyst on the molecular weight (boiling point) reduction and desulfurization of petroleum resids related to coal/petroleum resids coprocessing.

HT-SimDis is a useful tool for characterizing resids with boiling point up to about 770 °C, provided that proper GC conditions are used. HT-SimDis GC analysis can also be used to estimate the various boiling fractions of hydroprocessed resids in order to compare the efficiency of various catalysts at different temperature by comparing their boiling fractions.

Adding catalysts tested in this study is not very effective to reduce resid boiling point range but can achieve advantageous result with hydrodesulfurization at suitable conditions. ATTM and water did not show any promising synergistic effect on resid upgrading, although we have observed such promoting effects of water on the in-situ generated Mo sulfide catalyst in liquefaction of low rank coals such as Wyodak coal and in model compound reactions such as NMBB (in our earlier report to DOE) and DNE (first part of this report). These results may be an indication that cracking of aliphatic C-C bonds in the petroleum resids is thermally driven under upgrading and coprocessing conditions, and the cleavage of such aliphatic C-C bonds is not affected to any significant extent by the molybdenum sulfide catalysts. Such type of catalyst is effective for hydrodesulfurization of aromatic sulfur compounds.

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