COPROCESSING COAL WITH HYDROGENATED
VACUUM PYROLYZED TIRE OIL

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Abstract

A two-step coprocessing of waste rubber tires with a high volatile bituminous coal is advantageous. The first step involves pyrolyzing the waste rubber tires under vacuum at 600 °C. The condensed volatile material, called vacuum pyrolyzed tire oil (VPTO), is then used as a coal solvent. This solvent increases coal conversion to liquids by 20% when compared to coal conversion with waste rubber tire crumb. GC/MS and NMR analyses of the VPTO show the presence of non-hydrogen donor molecules, such as naphthalene, anthracene, phenanthrene, pyrene, and their methylated derivatives. Partial hydrogenations of VPTO were carried out using different types of presulfided hydrogenation catalysts, including Ni/Al_2O_3, $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, NiW/Al_2O_3, Ni/SiO_2-Al_2O_3, Pd/activated carbon, unsulfided Pt/Al_2O_3 and Pt/activated carbon. The hydrogenations of VPTO were also investigated under different temperatures and hydrogenation pressures when the catalyst was Ni/Al_2O_3. The hydrogenated products were characterized by NMR, GC, GC/MS and elemental analysis. The partially hydrogenated VPTO (HVPTO) products were then coprocessed with different coal ranks at different reaction temperatures and pressures with and without finely dispersed Mo naphthenate, $Mo(CO)_6$, $(NH_4)_2MoS_4$ and $Mo/Fe_2O_3/SO_4$ catalysts. Several model compounds were coprocessed with coal in order to make comparisons with the HVPTO.

Introduction

Solvent plays an important role in coal liquefaction processes. Two features are critical for a solvent to be effective. It must be a good physical solvent for coal products, and it must have H-donor or H-shuttling capacity in order to hydrogenate and stabilize free radicals derived from coal. For a commercial coal liquefaction plant a plentiful and economical supply of process solvent must be available. A possible answer is to utilize various waste oils as coal liquefaction solvents. Converting waste rubber tires back into vacuum pyrolyzed tire oil (VPTO) is one approach.[1-2] Williams and Taylor have shown depolymerization of tire polymer by pyrolysis produces butadiene and styrene products and fragments thereof.[3] The pyrolysis products then proceed through Diels-Alder type reactions to form cyclic compounds which dehydrogenate to yield aromatic molecules that are poor hydrogen donors.[4-5] These products facilitate coal dissolution during liquefaction, and increase coal conversion by 20 % when compared to coal conversion with rubber tire crumb.[2] McMillen and coworkers suggested that non-donor molecules aid in the cleavage of coal bonds.[6] Mochida *et al.*[7] and de Marco and coworkers[8] have shown that partial hydrogenation of non-donors to form H-donor molecules using a hydrogenation catalyst followed by processing the hydrogenated solvent with coal can be an effective method of coal liquefaction

In the present study, the objectives of hydrogenating VPTO were to (1) convert aromatic molecules (especially polyaromatic nondonors) in the oil to hydroaromatics with the capability of donating hydrogen; (2) crack some large polyaromatic molecules to lower molecular weight material that might serve as a better solvent; (3) reduce the coking effect generated by the large polyaromatic molecules; (4) eliminate the need for a disposable coal liquefaction catalyst, making the coprocessing more economical and (5) optimize coal conversion to liquids by coprocessing the partially hydrogenated VPTO (denoted HVPTO) with coals under a range of conditions.

Experimental

Materials. All coals (-60 mesh) were obtained from the Penn State Coal Bank and stored under nitrogen at 0 °C, including Blind Canyon (Utah) coal (DECS-6), Illinois #6 coal (DECS-2), Smith-Roland coal (DECS-8), Beulah coal (DECS-11), Pocahontas coal (DECS-19) and Wyodak-Anderson coal (DECS-26). The model compounds were obtained from Aldrich and used without further purification, including tetralin, naphthalene, pyrene, phenanthrene, anthracene and 9,10-dihydroanthracene. Oil obtained by vacuum pyrolysis of waste rubber tires was produced by Conrad Industries, Chehalis, WA. The VPTO was stored under ambient conditions. Properties of the VPTO

are listed in Table 1. Several hydrogenation catalysts were used on the VPTO, including Ni/Al$_2$O$_3$ (Harshaw), NiMo/Al$_2$O$_3$ (Katalco, 6.7% NiO% and 27.0% MoO$_3$), CoMo/Al$_2$O$_3$ (Nalco), NiMo/Al$_2$O$_3$ (Harshaw), NiMo/Al$_2$O$_3$ (5.4% NiO% and 20.0% MoO$_3$), Ni/SiO$_2$-Al$_2$O$_3$ (Harshaw), Pt/activated carbon (5%Pt, Alfa), Pt/Al$_2$O$_3$ (5%Pt, Alfa) and Pd/activated carbon (5% Pd, Alfa). Four finely dispersed catalytic systems were used for the coprocessing of HVPTO with coal: Mo naphthenate (ICN Biomedical Inc.), (NH$_4$)$_2$MoS$_4$ (Aldrich), Mo(CO)$_6$ (Aldrich) + S and Mo/Fe$_2$O$_3$/SO$_4$ + S (Prof. Wender's laboratory).

Hydrogenation of VPTO. All hydrogenation catalysts were presulfided at 350 °C for two hours except Pt catalysts. The presulfidation apparatus is shown in Figure 1. The hydrogenation experiments were completed using a well-stirred stainless-steel 150 cm^3 autoclave reactor (see Figure 2) under various reaction conditions for 1 h. Most reactions were carried out at 325 °C and 1000 psig of H$_2$(cold). During a typical hydrogenation run, the reactor was charged with 4 g freshly presulfided catalyst and 20 g of VPTO.The reactor was then sealed, purged with N$_2$ twice, and charged with 1000 psig (cold) of H$_2$. An electric furnace brought the reactants to the set point temperature at a rate of about 8 °C/min. At the end of the reaction time, measured from the time reaction temperature was reached, the reactor was cooled with a fan to room temperature. The gases were vented (H$_2$S was trapped by NaOH solution) and the hydrogenated liquids with solid catalyst were collected for further use or analyses. The separation of the liquid from the solid catalyst was completed by filtration with fritted glass filters (medium pore size).

Coal-VPTO or HVPTO Coprocessing. Coprocessing experiments were carried out in 27 cm^3 horizontal tubing reactors. Reactants were brought to the set-point temperature, usually within 10 min, by immersing the reactor in a preheated fluidized sand bath. The reactor was shaken horizontally (3 times/s) to ensure adequate mixing. At the end of a 1 h reaction time, the reactor was removed from the sand bath and allowed to cool at room temperature for 5 mins, and quenched in cold water. Reaction products and solids were removed and extracted with THF, and then the solvent was removed with a rotary evaporator. The THF soluble portion was dried under vacuum for two hours and weighed. The THF insoluble residue remaining in the Soxhlet extractor thimble was also dried for two hours under vacuum. The dried THF solubles were then extracted with cyclohexane. The cyclohexane was removed from the oil sample using a rotary evaporator. The cyclohexane insoluble residue is referred to as asphaltenes. The cyclohexane soluble portion is referred to as oil. (NH$_4$)$_2$MoS$_4$ was used as received to impregnate the coal from aqueous solution by the incipient wetness technique. Mo naphthenate was dissolved in HVPTO and then mixed with the coal to get a fine dispersion. Mo(CO)$_6$ (Aldrich) + S was ground to a fine powder and then mixed up with the coal. Mo/Fe$_2$O$_3$/SO$_4$ was calcined at 550 °C for approximately 2.5 hours before use. All four of the catalysts were used with 1% by weight presence of Mo or its equivalent (for Mo/Fe$_2$O$_3$/SO$_4$ system).

Reactant and Product Characterization Techniques. GC-MS analyses were completed on a Hewlett-Packard 5890 series II gas chromatograph coupled to a Hewlett-Packard 5971 mass spectrometer. A J & W 100 meter DB-1 column was used for the GC-MS analyses. Elemental analyses were completed by Atlantic Microlabs, Norcross, Georgia. ^{1}H NMR analyses were completed on a Varian XL-300 NMR spectrometer, and CDCl$_3$ with 1% TMS (tetramethylsilane) was used as solvent.

Total conversion of coal and conversions to product fractions were defined on an ash-free basis as follows :

coal conversion: $Y_T = 100(1-Y)$; $Y = (W_I - W_C - W_{ash})/W_{maf}$
conversion to asphaltenes: $Y_A = 100(W_A/W_{maf})$
conversion to oils and gases: $Y_{O+G} = 100(Y_T - Y_A)$

where W_I, W_c, W_{ash}, W_A and W_{maf} are masses of THF insoluble products, catalyst, ash, asphaltenes and moisture- and ash-free coal; Y_T, Y_A, and Y_{O+G} denote total, asphaltenes and gas + oil yields, respectively.

Results and Discussion

Hydrogenation of VPTO

An ideal hydrogenated VPTO would serve as both a good solvent and a good hydrogen donor during processing with coal. That means that one should seek a suitable hydrogenation catalyst under proper reaction conditions to convert the polyaromatic molecules to partially hydrogenated ones, e.g., converting naphthalene to tetralin instead of decalin. Our GC/MS (Fig. 3a) and ^{1}H NMR (Fig. 4a) analyses show a high percentage of non-donor aromatic molecules in VPTO, such as benzene, naphthalene, anthracene, phenanthrene, pyrene, and their methylated derivatives. Seeking to achieve mild hydrogenation, different types of presulfided hydrogenation catalysts were tested at 325 °C and 1000 psig of H$_2$ (cold) for 1 h, including Ni/Al$_2$O$_3$, CoMo/Al$_2$O$_3$, NiMo/Al$_2$O$_3$, NiW/Al$_2$O$_3$, Ni/SiO$_2$-

Al$_2$O$_3$, Pd/activated carbon, unsulfided Pt/Al$_2$O$_3$ and Pt/activated carbon. Hydrogenation of VPTO was also investigated at different temperatures and hydrogenation pressures when the catalyst was Ni/Al$_2$O$_3$. NMR, GC and GC/MS data indicate that the degree of hydrogenation depends not only on the catalysts used but also on the reaction temperature and H$_2$ pressure. We found that NiMo/Al$_2$O$_3$ (6.7% NiO and MoO$_3$) and Ni/Al$_2$O$_3$ are the best catalysts, and 325 °C and 1000 psig of H$_2$ (cold) are the optimum reaction conditions for the subsequent coprocessing of HVPTO with coal. Two typical ^{1}H NMR spectra of HVPTO are shown in Fig. 3b (Pt/Al$_2$O$_3$, 325 °C and 1000 psig of H$_2$) and 3c (Ni/Al$_2$O$_3$, 325 °C and 2000 psig of H$_2$). GC/MS data shown in Figs. 4a and 4b indicate that many polyaromatic molecules were changed to hydroaromatics, e.g. methylated derivatives of naphthalene were converted to those of tetralin.

Effect of Hydrogenation Catalysts

Figure 5 shows the effect of using nine different hydrogenation catalysts (A: Ni/Al$_2$O$_3$; B: CoMo/Al$_2$O$_3$; C: NiW/Al$_2$O$_3$; D: NiMo/Al$_2$O$_3$ (6.7% of NiO and 27%MoO$_3$); E: NiMo/Al$_2$O$_3$ (5.4% of NiO and 20%MoO$_3$); F: Pt/Al$_2$O$_3$; G: Pt/Carbon; H: Pd/Carbon and I: Ni/SiO$_2$-Al$_2$O$_3$) in preparing HVPTO (Hydrogenation conditions: 325 °C, 1 h and 1000 psig of H$_2$ (cold)) on the coal conversions of the the subsequent stage, when Blind Canyon coal was coprocessed with the hydrogenated oils without coal liquefaction catalysts at 430 °C and 1000 psig of H$_2$ (cold) for 1 h. For comparison purposes the coprocessing of Blind Canyon coal with unhydrogenated VPTO was also carried out under the same reaction conditions (represented by column J). Differences in the effects of hydrogenation catalysts on the coal conversion are not large from one catalyst to another and vary in the following order: NiMo/Al$_2$O$_3$ (D, 67.1%) > Ni/Al$_2$O$_3$ (A, 63.8%) > NiW/Al$_2$O$_3$ (C, 61.6%) ~ Pt/Carbon (G, 61.1%) ~CoMo/Al$_2$O$_3$ (B, 59.8%) > NiMo/Al$_2$O$_3$ (E, 57.2%) > Pt/Al$_2$O$_3$ (F, 55.7%) > Pd/Carbon (H, 50.3%) ~ Ni/SiO$_2$-Al$_2$O$_3$ (I, 50.2%) > No catalyst,VPTO (J, 34.1%). The coal conversion yield does indirectly reflect the hydrogenation behavior. The highest conversions for NiMo/Al$_2$O$_3$ (6.7% of NiO and 27% of MoO$_3$) and Ni/Al$_2$O$_3$ mean that they convert the polyaromatics to hydrogen donor-rich hydroaromatics to the optimum extent. It is not surprising that the conversion yield for the coprocessing of VPTO with Blind Canyon coal is the lowest (roughly half of the highest conversion) because no hydroaromatics are present in VPTO. The advantage of the hydrogenation pretreatment over unhydrogenated VPTO for the coprocessing is proven conclusively.

Comparison Between Model Compounds and the Hydrogenated VPTO

Figure 6 shows the comparison of HVPTO (hydrogenated by Ni/Al$_2$O$_3$) as solvent with six model compounds, when coprocessed with Blind Canyon coal without a coal liquefaction catalyst. It can be seen that naphthalene, anthracene, phenanthrene and pyrene, which are polyaromatic compounds, give relatively low coal conversions (<52%), due to their non-donor character. The low but still significant conversions obtained with these solvents must be attributed either to direct interaction of H$_2$ with coal or to H-shuttling reactions in which solvent transfers hydrogen to coal from the gas phase or from hydrogen-rich portions of coal. On the other hand, HVPTO like tetralin and 9,10-dihydroanthracene, which are hydroaromatic compounds, gives a relatively high liquefaction yield (HVPTO (63.8%) < 9,10-dihydroanthracene (66.0%) < tetralin (69.1%)). These results are consistent with the strong H-donor capacity of these model compounds.

Influence of the Hydrogenation Temperatures and Pressures

The effects of hydrogenation temperatures and pressures on the coprocessing of HVPTO with Blind Canyon coal (without a coal liquefaction catalyst) at 430 °C are shown in Fig. 7 and Fig. 8, respectively. Figure 7 indicates that when the hydrogenation temperature is 325 °C the highest coal conversion can be obtained (40.9% at 400 °C < 54.3% at 170 °C < 55.2% at 260 °C < 63.8% at 325 °C). Figure 8 shows that when H$_2$ pressure is 1000 psig (cold), coal conversion is better than when H$_2$ pressure is either 500 psig (cold) or 1500 psig (cold). Therefore, hydrogenation at 325 °C and 1000 psig of H$_2$ (cold) are the optimum reaction conditions. HVPTO obtained at these optimum hydrogenation conditions was used in the subsequent studies. These results are supported by Demirel's detailed hydrogenation studies of polyaromatics.[9]

Effect of the Rank of Coals

Coal conversion values as a function of coal ranks, when the coal was coprocessed with the HVPTO hydrogenated by Ni/Al$_2$O$_3$ without a coprocessing catalyst are reported in Fig. 9. The coals are listed according to rank with Pocahontas the highest ranking coal and Beulah the coal of lowest rank. The conversions vary as follows: Illinois #6 (81.9%) > Smith-Roland (68.0%) > Wyodak-

Anderson (65.1%) > Blind Canyon (63.8%) > Beulah (52.9%) > Pocahontas (49.5%). The data indicate that the coal conversion has no correlation with coal rank when the coals are coprocessed with HVPTO. Illinois #6 coal has the largest proportion of sulfur and iron oxide among all six coals. These two substances combine to form pyrite or pyrrhotite which can then act as a catalyst. Thus, Illinois #6 coal shows the highest conversion. Pocahontas has a high fixed carbon content and a low volatile matter content and thus is unreactive. We chose Blind Canyon coal for the coprocessing investigations because it has the lowest percentage of sulfur and iron.

Effects of Coal Liquefaction Catalysts and Coprocessing Temperatures

The comparison of the coprocessing of HVPTO (hydrogenated by Ni/Al_2O_3) and VPTO with or without coal liquefaction catalysts at 430 °C and 350 °C is reported in Fig. 10 and Fig. 11, respectively. In either Fig. 10 or Fig. 11, the catalytic effect is obvious, especially when $(NH_4)_2MoS_4$ or $Mo/Fe_2O_3/SO_4$ + S were used. These two catalysts increased the coal conversion to 94.2% and 91.3% from 63.8% without coal liquefaction catalyst at 430 °C. The incipient wetness technique for the $(NH_4)_2MoS_4$ impregnation provided a very fine catalyst dispersion, which is probably the reason why it yielded the highest conversion. The high conversion obtained from the $Mo/Fe_2O_3/SO_4$ + S system is possibly due to the superacid structure of the catalyst, which increased the cracking or hydrocracking of coal considerably compared to other catalysts, such as $Mo(CO)_6$ + S and Mo naphthenate. When the coprocessing temperature was increased from 350 °C to 430 °C, the conversion for HVPTO without catalyst increased from 53.9% to 63.8%, but conversions with $(NH_4)_2MoS_4$ and $M(CO)_6$ + S as catalysts increased from 59.1% and 73.8 % to 70.1% and 94.2%, respectively.

Conclusions

Hydrogenated VPTO (HVPTO) is a much better solvent than unhydrogenated VPTO for coprocessing with coal, but no effect of varying coal rank is observed. $NiMo/Al_2O_3$ (6.7% of NiO and 27% MoO_3) and Ni/Al_2O_3 are the best catalysts for converting polyaromatics to hydrogen donor-rich hydroarmatics among nine tested catalysts. 325 °C and 1000 psig of H_2 (cold) are the optimum hydrogenation conditions. While HVPTO is a better solvent for coprocessing compared to non-donor polyaromatic model compounds, it is not as good as strong H-donor model compounds such as tetralin and 9,10- dihydroanthracene. $(NH_4)_2MoS_4$ and $Mo/Fe_2O_3/SO_4$ are excellent coal liquefaction catalysts when HVPTO is coprocessed with coal.

Acknowlegements

References

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Table 1. Properties of vacuum pyrolyzed tire oil (VPTO)
provided by Conrad Industries, Chehalis, WA.

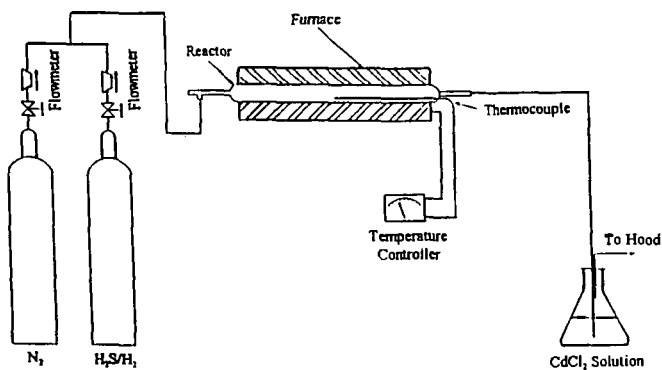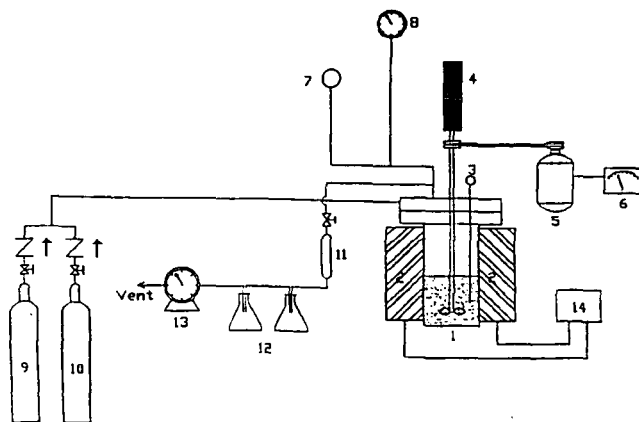|	
C, wt%	87.7
H, wt%	11.0
S, wt%	0.6
N, wt%	0.3
O, wt%	0.4
atomic H/C	1.51
Zn	40 ppm
cyclohexane insolubles	5.2%

Figure 1. Hydrogenation catalyst presulfidation unit, cited from Ref. 9

Figure 2. Autoclave reactor assembly for the hydrogenation experiments, cited from Ref. 9.
1: Reactor; 2: Heating jacket; 3: Thermocouple; 4: Magnetic drive assembly; 5: Motor;
6: Stirrer controller; 7: Emergency dump; 8: Pressure gauge; 9: Nitrogen cylinder; 10: Hydrogen
cylinder; 11: Gas sample collector; 12: H$_2$S trap; 13: Wet flow meter and 14: Temperature controller
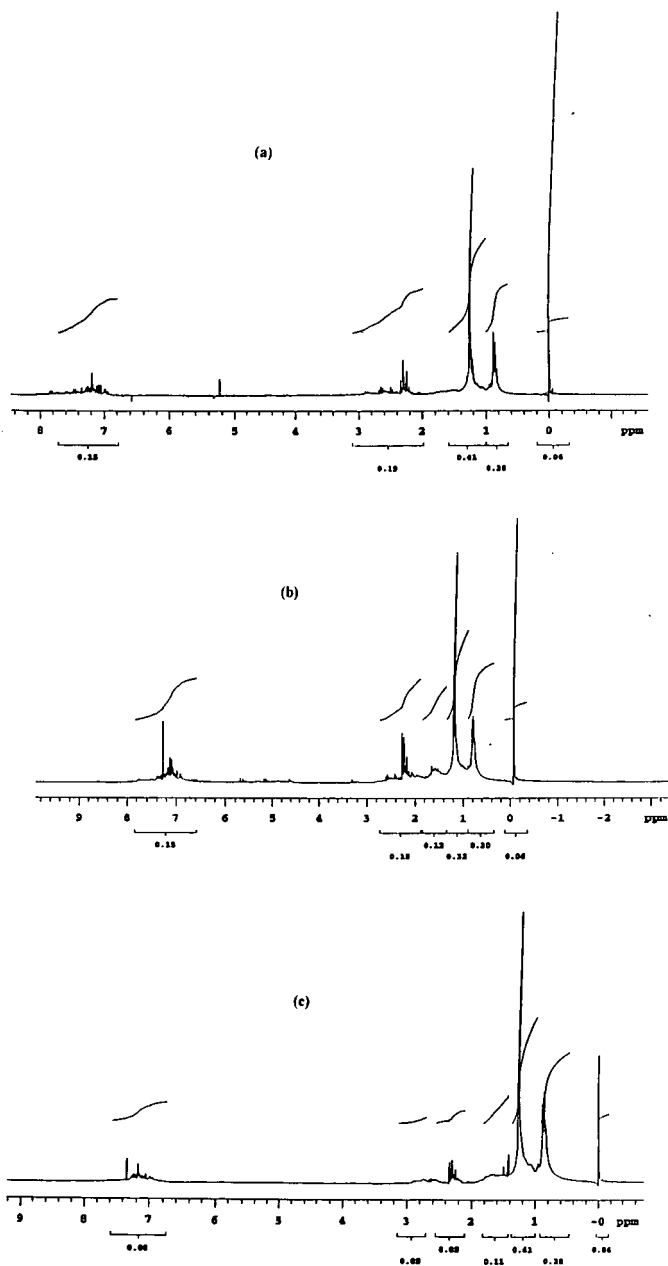
Figure 3. 300 MHz ^{1}H NMR spectra of VPTO and HVPTO (CDCl$_3$ with 1% TMS used as solvent). (a): VPTO; (b): HVPTO by Pt/Al$_2$O$_3$ at 325 °C, 1 h and 1000 psig of H$_2$ (cold) and (c): HVPTO by Ni/Al$_2$O$_3$ at 325 °C, 1 h and 2000 psig of H$_2$ (cold).
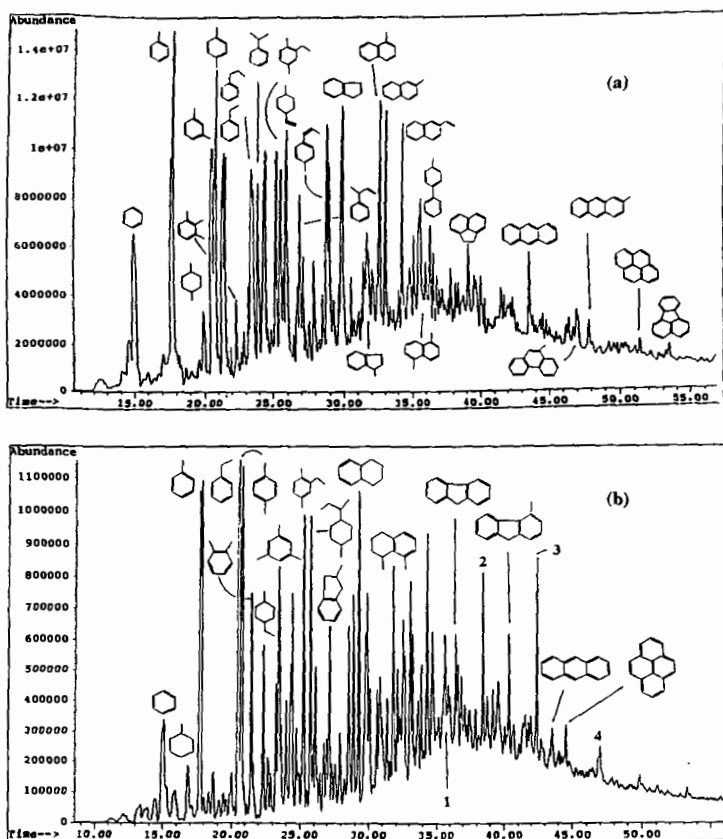
Figure 4. GC/MS analyses of VPTO and HVPTO. (a): VPTO and (b): HVPTO by Ni/Al$_2$O$_3$ at 325 °C, 1 h and 1000 psig of H$_2$ (cold). 1: Dodecane, 2-methyl-6-propyl; 2: Hexadecane; 3: Octadecane and 4: Heptadecane
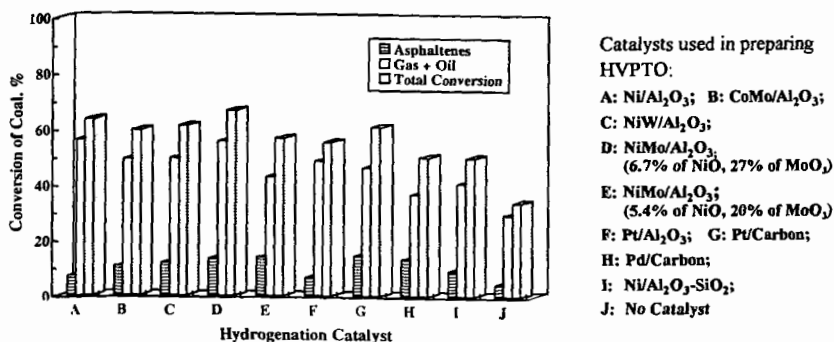

Catalysts used in preparing HVPTO:

A: Ni/Al$_2$O$_3$; B: CoMo/Al$_2$O$_3$;
C: NiW/Al$_2$O$_3$;
D: NiMo/Al$_2$O$_3$; (6.7% of NiO, 27% of MoO$_3$)
E: NiMo/Al$_2$O$_3$; (5.4% of NiO, 20% of MoO$_3$)
F: Pt/Al$_2$O$_3$; G: Pt/Carbon;
H: Pd/Carbon;
I: Ni/Al$_2$O$_3$-SiO$_2$;
J: No Catalyst

Figure 5. Effect of using nine different hydrogenation catalysts in preparing HVPTO. The catalysts indicated on the right (A, B, etc.) were used to prepare the HVPTO (Hydrogenation conditions: VPTO, 325 °C, 1 h and 1000 psig of H$_2$ (cold)). Then the resulting HVPTO was coprocessed with Blind Canyon coal with no catalyst present. (Coprocessing conditions: Blind Canyon coal with HVPTO or VPTO, 430 °C, 1 h, 1000 psig of H$_2$ (cold) and m$_{HVPTO}$/m$_{coal}$ = 2g/2g). The last column (J) represents coprocessing of VPTO with Blind Canyon coal.

Comparison of HVPTO with model compounds

A: HVPTO/Ni/Al₂O₃
B: Tetralin
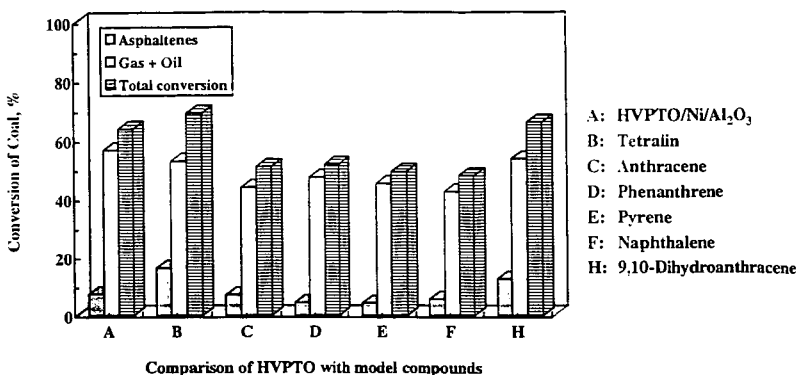C: Anthracene
D: Phenanthrene
E: Pyrene
F: Naphthalene
H: 9,10-Dihydroanthracene

Figure 6. Comparison of HVPTO (hydrogenated by Ni/Al$_2$O$_3$ at 325 °C, 1 h and 1000 psig of H$_2$ (cold)) as solvent with several model compounds for the coprocessing with Blind Canyon coal. (Coprocessing conditions: 430 °C, 1 h, no catalyst, 1000 psig of H$_2$ and m$_{solvent}$/m$_{coal}$: 2g/2g)

Figure 7. Effect of hydrogenation temperatures on the second stage of coal liquefaction.
Hydrogenation conditions:
  VPTO
  Ni/Al$_2$O$_3$ as catalyst,
  1 h
  1000 psig of H$_2$ (cold)
Coprocessing conditions:
Blind Canyon coal
  HVPTO
  430 °C and 1 h
  1000 psig of H$_2$ (coal)
  m$_{HVPTO}$/m$_{coal}$ = 2g/2g
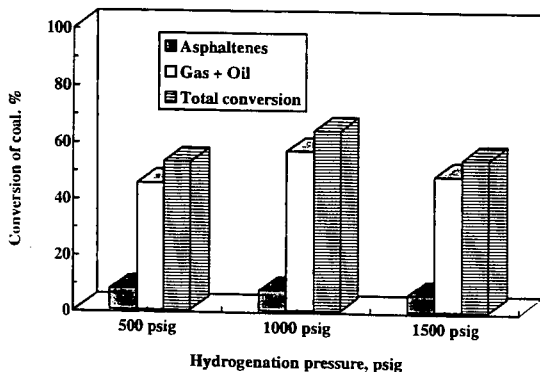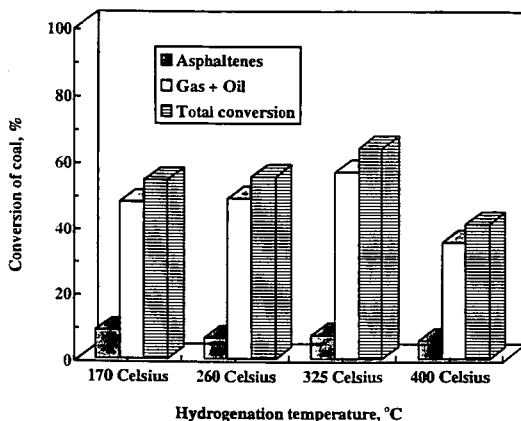

Figure 8. Effect of hydrogenation pressures on the second stage of coal liquefaction.
Hydrogenation conditions:
  VPTO
  Ni/Al$_2$O$_3$ as catalyst
  1 h and 325 °C
Coprocessing conditions:
  Blind Canyon coal
  HVPTO
  430 °C and 1 h
  1000 psig of H$_2$ (cold)
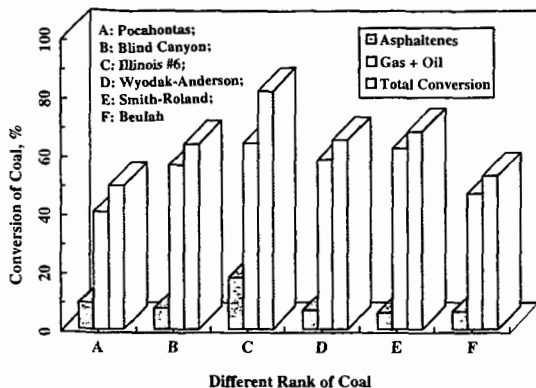 m$_{HVPTO}$/m$_{coal}$ = 2g/2g

Figure 9. Effect of different ranks of coal on the second stage of coal liquefaction. Hydrogenation conditions:
VPTO
    Ni/Al$_2$O$_3$ as catalyst
    1 h and 325 °C
    1000 psig of H$_2$ (cold)
Coprocessing conditions:
    Blind Canyon coal
    HVPTO
    1 h and 430 °C
    1000 psig of H$_2$ (cold)
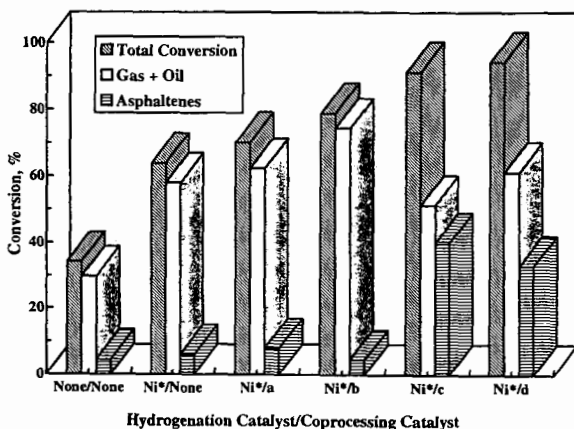 m_{HVPTO}/m_{coal} = 2g/2g

Figure 10. Effect of coal liquefaction catalysts on the coprocessing of HVPTO (hydrogenated by Ni/Al$_2$O$_3$ at 325 °C, 1 h and 1000 psig of H$_2$ (cold)) with Blind Canyon coal.
Coprocessing conditions: 430 °C, 1 h, 1000 psig of H$_2$ (cold) and m_{oil}/m_{coal}: 2g/2g
Ni* ≡ Ni/Al$_2$O$_3$; a: Mo(CO)$_6$ + S; b: Mo naphthenate; c: Mo/Fe$_2$O$_3$/SO$_4$ + S; d: (NH$_4$)$_2$MoS$_4$

Figure 11. Effect of coal liquefaction catalysts on coprocessing of HVPTO with Blind Canyon coal at 350 °C.
Hydrogenation conditions:
    Ni/Al$_2$O$_3$ as catalyst
    325 °C and 1 h
    1000 psig of H$_2$ (cold)
Coprocessing conditions:
    350 °C and 1 h
    1000 psig of H$_2$ (cold)
    m_{oil}/m_{coal}: 2g/2g)
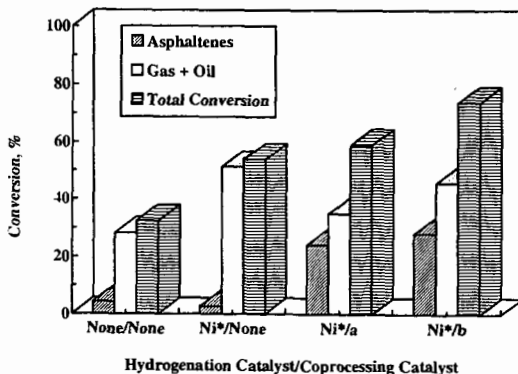
Ni* ≡ Ni/Al$_2$O$_3$
a: Mo(CO)$_6$ + S; b: (NH$_4$)$_2$MoS$_4$

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