COPROCESSING COAL WITH HYDROGENATED VACUUM PYROLYZED TIRE OIL

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Keywords: coprocessing, vacuum pyrolyzed tire oil, hydrogenation, coal

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/Al₂O₃, CoMo/Al₂O₃, NiMo/Al₂O₃, NiW/Al₂O₃, Ni/SiO₂-Al₂O₃, Pt/activated carbon, unsulfided Pt/Al₂O₃, and Pt/activated carbon. The hydrogenations of VPTO were also investigated under different temperatures and hydrogenation pressures when the catalyst was Ni/Al₂O₃. 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)₉, (NH₃)ₓMoSₓ, and Mo/FeₓOₙ/SO₄ 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. Williams and Taylor have shown depolymerization of tire polymer by pyrolysis produces butadiene and styrene products and fragments thereof. 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. These products facilitate coal dissolution during liquefaction, and increase coal conversion by 20% when compared to coal conversion with rubber tire crumb. McMillen and coworkers suggested that non-donor molecules aid in the cleavage of coal bonds. Mochida et. al. and de Marco and coworkers 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/Al₂O₃ (Harshaw), NiMo/Al₂O₃ (Katalco, 6.7% NiO% and 27.0% MoO₃), CoMo/Al₂O₃ (Naica), NiMo/Al₂O₃ (Harshaw), NiMo/Al₂O₃ (5.4% NiO% and 20.0% MoO₃), Ni/SiO₂-Al₂O₃ (Harshaw), Pt/activated carbon (5%Pt, Alfa), Pt/Al₂O₃ (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.), (NH₄)₂MoS₄ (Aldrich), Mo(CO)₆ (Aldrich) + S and Mo/Fe₂O₃/So₃ + 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 cm³ autoclave reactor (see Figure 2) under various reaction conditions for 1 h. Most reactions were carried out at 325 °C and 1000 psig of H₂(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 N₂, and charged with 1000 psig (cold) of H₂. 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 (H₂S 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 cm³ 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 h. 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. (NH₄)₂MoS₄ 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/Fe₂O₃/So₃ 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/Fe₂O₃/So₃ 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. ¹H NMR analyses were completed on a Varian XL-300 NMR spectrometer, and CDCl₃ with 1% TMS (tetramethylsilane) was used as solvent. The total conversion of coal and conversions to product fractions were defined on an ash-free basis as follows:
coal conversion:  Yₕ = 100(1-Yₚ);  Yₚ = (Wₕ - Wₚ - Wₘₜ)/Wₘₜ
conversion to asphaltenes:  Yₐ = 100(Wₐ)/Wₘₜ
conversion to oils and gases:  Yₒ + g = 100(Yₕ - Yₚ - Yₐ)
where Wₕ, Wₚ, Wₘₜ, Wₐ and Wₒ+g are masses of THF insoluble products, catalyst, ash, asphaltenes and moisture- and ash-free coal; Yₕ, Yₚ and Yₒ+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 ¹H 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 H₂ (cold) for 1 h, including Ni/Al₂O₃, CoMo/Al₂O₃, NiMo/Al₂O₃, NiW/Al₂O₃, Ni/SiO₂-Al₂O₃, and NiMo/Al₂O₃ (Katalco, 6.7% NiO% and 27.0% MoO₃), CoMo/Al₂O₃ (Naica), NiMo/Al₂O₃ (Katalco, 6.7% NiO% and 27.0% MoO₃), Ni/SiO₂-Al₂O₃ (Harshaw), Pt/activated carbon (5%Pt, Alfa), Pt/Al₂O₃ (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.), (NH₄)₂MoS₄ (Aldrich), Mo(CO)₆ (Aldrich) + S and Mo/Fe₂O₃/So₃ + S (Prof. Wender's laboratory).
Al₂O₃, Pd/activated carbon, unsulfided Pt/Al₂O₃, and Pt/activated carbon. Hydrogenation of VPTO was also investigated at different temperatures and hydrogenation pressures when the catalyzer was Ni/Al₂O₃. 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 H₂ pressure. We found that NiMo/Al₂O₃ (6.7% NiO and MoO₃) and Ni/Al₂O₃ are the best cataylsts, and 325 °C and 1000 psig of H₂ (cold) are the optimum reaction conditions for the subsequent coprocessing of HVPTO with coal. Two typical ¹H NMR spectra of HVPTO are shown in Fig. 3b (Pt/Al₂O₃, 325 °C and 1000 psig of H₂) and 3c (Ni/Al₂O₃, 325 °C and 2000 psig of H₂). 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/Al₂O₃; B: CoMo/Al₂O₃; C: NiW/Al₂O₃; D: NiMo/Al₂O₃ (6.7% of NiO and 27% of MoO₃); E: NiMo/Al₂O₃ (5.4% of NiO and 20%MoO₃); F: Pt/Al₂O₃; G: Pt/Carbon; H: Pd/Carbon and I: Ni/SiO₂-Al₂O₃) in preparing HVPTO (Hydrogenation conditions: 325 °C, 1 h and 1000 psig of H₂ (cold)) on the coal conversions of the subsequent stage, when Blind Canyon coal was coprocessed with the hydrogenated oils without coal liquefaction catalysts at 430 °C and 1000 psig of H₂ (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/Al₂O₃ (D, 67.1%) > Ni/Al₂O₃ (A, 63.8%) > NiW/Al₂O₃ (C, 61.6%) > Pt/Carbon (G, 61.1%) > CoMo/Al₂O₃ (B, 59.8%) > NiMo/Al₂O₃ (E, 57.2%) > Pt/Al₂O₃ (F, 55.7%) > Pd/Carbon (H, 50.3%) > N/SiO₂-Al₂O₃ (I, 50.2%) > No catalyst, VPTO (J, 34.1%). The coal conversion yield does indirectly reflect the hydrogenation behavior. The highest conversions for NiMo/Al₂O₃ (6.7% of NiO and 27% of MoO₃) and Ni/Al₂O₃ 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 VPTO (hydrogenated by Ni/Al₂O₃) 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 H₂ 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 H₂ pressure is 1000 psig (cold), coal conversion is better than when H₂ pressure is either 500 psig (cold) or 1500 psig (cold). Therefore, hydrogenation at 325 °C and 1000 psig of H₂ (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.

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/Al₂O₃ 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/Al₂O₃) 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 (NH₄)₂MoS₄ or Mo/Fe₂O₃/SO₃ + 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 (NH₄)₂MoS₄ 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/Fe₂O₃/SO₃ + 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 (NH₄)₂MoS₄ and Mo/Fe₂O₃/SO₃ were used. These two 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/Al₂O₃ (6.7% of NiO and 27% MoO₃) and Ni/Al₂O₃ are the best catalysts for converting polyaromatics to hydrogen donor-rich hydroaromatics among nine tested catalysts. 325 °C and 1000 psig of H₂ (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. (NH₄)₂MoS₄ and Mo/Fe₂O₃/SO₃ are excellent coal liquefaction catalysts when HVPTO is coprocessed with coal.

Acknowledgements

We gratefully acknowledge Philip Bridges of Conrad Industries, Chehalis, WA for his generous donation of vacuum pyrolyzed tire oil. We are also grateful to Professor Joseph S. Shabtai (Department of Chemical and Fuels Engineering, University of Utah) for allowing us to use his autoclave reactor and for very helpful discussions. Special thanks go to Dr. Xin Xiao (Department of Chemical and Fuels Engineering, University of Utah) for some technical assistance with the hydrogenation experiments. The donation of a coal liquefaction catalyst (Mo/Fe₂O₃/SO₃) by Prof. Irving Wender (Department of Chemical and Petroleum Engineering, University of Pittsburgh) is also greatly appreciated. Financial support by the U.S. Department of Energy, Fossil Energy Division, through the Consortium for Fossil Fuel Liquefaction Sciences, Contract No. UKRF-4-21033-86-24, is gratefully acknowledged.

References

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

<table>
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<th>Property</th>
<th>Value</th>
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<tr>
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<tr>
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<tr>
<td>Zn, ppm</td>
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<tr>
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Figure 1. Hydrogenation catalyst presulfidation unit, cited from Ref. 9.

Figure 2. Autoclave reactor assembly for the hydrogenation experiments, cited from Ref. 9.
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).
Catalysts used in preparing HVPTO:
A: NiAl₂O₃; B: CoMo/Al₂O₃;
C: NiW/Al₂O₃;
D: NiMo/Al₂O₃;
(5.7% of NiO, 21% of MoO₃)
E: NiMo/Al₂O₃;
(5.4% of NiO, 20% of MoO₃)
F: Pt/Al₂O₃; G: Pt/Carbon;
H: Pd/Carbon;
I: NiAl₂O₃·SiO₂;
J: No Catalyst

Figure 4. GC/MS analyses of VPTO and HVPTO. (a): VPTO and (b): HVPTO by Ni/Al₂O₃ at 325 °C, 1 h and 1000 psig of H₂ (cold). 1: Dodecane, 2-methyl-6-propyl; 2: Hexadecane; 3: Octadecane and 4: Heptadecane

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 H₂ (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 H₂ (cold) and mHVPTO/mcoal = 2g/2g). The last column (J) represents coprocessing of VPTO with Blind Canyon coal.
Figure 6. Comparison of HVPTO (hydrogenated by Ni/Al₂O₃ at 325 °C, 1 h and 1000 psig of H₂ (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 H₂ and m_{solvant}/m_{coal} = 2g/2g)

Figure 7. Effect of hydrogenation temperatures on the second stage of coal liquefaction.
Hydrogenation conditions:
VPTO
Ni/Al₂O₃ as catalyst,
1 h
1000 psig of H₂ (cold)
Coprocessing conditions:
Blind Canyon coal
HVPTO
430 °C and 1 h
1000 psig of H₂ (coal)

m_{HVPTO}/m_{coal} = 2g/2g

Figure 8. Effect of hydrogenation pressures on the second stage of coal liquefaction.
Hydrogenation conditions:
VPTO
Ni/Al₂O₃ as catalyst
1 h and 325 °C
Coprocessing conditions:
Blind Canyon coal
HVPTO
430 °C and 1 h
1000 psig of H₂ (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/Al₂O₃ as catalyst
1 h and 325 °C
1000 psig of H₂ (cold)

Coprocessing conditions:

Blind Canyon coal
HVPTO
1 h and 430 °C
1000 psig of H₂ (cold)

\[ \frac{m_{HVPTO}}{m_{coal}} = 2g/2g \]

Figure 10. Effect of coal liquefaction catalysts on the coprocessing of HVPTO (hydrogenated by Ni/Al₂O₃ at 325 °C, 1 h and 1000 psig of H₂ (cold)) with Blind Canyon coal.
Coprocessing conditions: 430 °C, 1 h, 1000 psig of H₂ (cold) and \[ \frac{m_{HVPTO}}{m_{coal}} = 2g/2g \]

Ni* NI/Al₂O₃; a: Mo(CO)₆ + S; b: Mo naphthenate; c: Mo/Fe₂O₃/SO₃ + S; d: (NH₄)₂MoS₄

Figure 11. Effect of coal liquefaction catalysts on coprocessing of HVPTO with Blind Canyon coal at 350 °C.
Hydrogenation conditions:

Ni/Al₂O₃ as catalyst
325 °C and 1 h
1000 psig of H₂ (cold)

Coprocessing conditions:

350 °C and 1 h
1000 psig of H₂ (cold)

\[ \frac{m_{HVPTO}}{m_{coal}} = 2g/2g \]

Ni* NI/Al₂O₃

a: Mo(CO)₆ + S; b: (NH₄)₂MoS₄