DEVELOPMENT OF CONTINUOUS SOLVENT EXTRACTION PROCESSES FOR COAL DERIVED CARBON PRODUCTS

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ABSTRACT

The purpose of this DOE-funded effort is to develop continuous processes for solvent extraction of coal for the production of carbon products. These carbon products include materials used in metals smelting, especially in the aluminum and steel industries, as well as porous carbon structural material referred to as "carbon foam" and carbon fibers.

During this reporting period, efforts have focused on the development of continuous processes for hydrogenation as well as continuous production of carbon foam and coke.

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1.0 EXECUTIVE SUMMARY

The purpose of this DOE-funded effort is to develop continuous processes for solvent extraction of coal for the production of carbon products. These carbon products include materials used in metals smelting, especially in the aluminum and steel industries, as well as porous carbon structural material referred to as "carbon foam" and carbon fibers.

During this reporting period, efforts have focused on the development of continuous processes for hydrogenation as well as continuous production of carbon foam and coke.

The results of coal conversion using mild hydrotreatment, performed with two as-received coal-derived solvents HCO (Heavy Creosote Oil) and CBB (Carbon Black Base), their hydrogenated forms, and the recovered forms are compared. The five main goals of this research are:

a. To determine the effectiveness of the two solvents in the coal digestion reaction.

b. To investigate the effectiveness of the hydrotreatment reaction residue (unconverted coal) and NiO/ MiO_3 as catalysts in the solvent hydrogenation.

c. To investigate the effectiveness of the hydrogenated forms of both the solvents in the coal digestion reaction.

d. To study the effectiveness of recycled solvent as a hydrogen donor solvent in the coal digestion reaction.

e. To assess the converted coal product for use as a pitch or coke feedstock.

2.0 TECHNICAL

The results of coal conversion using mild hydrotreatment, performed with two as-received coal-derived solvents HCO (Heavy Creosote Oil) and CBB (Carbon Black Base), their hydrogenated forms, and the recovered forms are compared. The five main goals of this research are:

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d. To study the effectiveness of recycled solvent as a hydrogen donor solvent in the coal digestion reaction.

e. To assess the converted coal product for use as a pitch or coke feedstock.

The baseline reaction conditions were established in 2003, in order to permit a systematic study. Subsequently, the conditions were modified for use at the Hydro Treatment facility; the latter were modified, as shown in Table 1. In addition, the high solvent-to-coal ratio has the advantage of producing more recovered solvent, which can be further used to study the effectiveness of these recycled solvents as a potential hydrogen donor solvent for the coal digestion reactions.

Table 1. Baseline Parameters for the Lab Scale Study and in the Digestion Reactor.

Parameter	This Study	Digestion Reactor
Temperature	400 ^{o}C	425 ^{o}C
Pressure 400	500 psig	500 psig
Solvent to Coal Mass Ratio	5:1	3:1
Reaction Time	1 hour	1 Hour

Solvents were characterized on their ability to convert coal into THF solubles. The effectiveness is measured in terms of overall conversion and coal-alone conversion given by the following equations respectively.

$$\%\,\text{Overall Conversion} = \frac{[(\text{Mass of Raw Coal} + \text{Mass of Solvent}) - (\text{Mass of THF Insolubles})]}{\text{Mass of Raw Coal} + \text{Mass of Solvent}} \times 100$$

$$\% \text{ Coal - alone Conversion (daf)} = \frac{[(\text{Mass of Dry Coal}) - (\text{Mass of THF Insolubles})]}{\text{Mass of Coal (daf)}} \times 100$$

The main difference between these two calculations is that the overall conversion takes into account the coal and the solvent, while the coal-alone basis takes into account only the conversion of the coal.

The effect of temperature on solvent CBB (neat and hydrogenated) was studied by varying the reaction base-case temperature of 400 °C by $\pm$ 50 °C. The effect of the reaction atmosphere was also studied by conducting the same hydrotreatment reaction in both N_2 and H_2 atmospheres, keeping all other reaction conditions identical. Also, the effectiveness of the recovered hydrogenated CBB solvent for use as a hydrogenation solvent in hydrotreatment of coal is discussed. Finally, ash content, coke yield, softening temperature and optical texture of the recovered hydrogenation pitch products from all the reactions are discussed.

2.1 Solvent Hydrogenation

The pressure profiles of solvent hydrogenation of Carbon Black Base (CBB) and Heavy Creosote Oil (HCO) are shown below. The solvent CBB was hydrogenated at 350°C and 500 psig (cold) pressure using NiO/MiO_3 as the catalyst. The solvent HCO was hydrogenated at 400°C and 500 psig (cold) pressure using the unconverted coal as the catalyst. The unconverted coal used as the catalyst was obtained from the hydrotreatment reaction of coal with the same solvent HCO. As can be seen below, there is a difference in initial and final cold pressures of hydrogen indicating the consumption of hydrogen by the solvent during the process. The drop in pressure is much more significant for the solvent CBB than that for HCO even though HCO was hydrogenated at a slightly higher temperature than the solvent CBB. The less significant decrease in hydrogen pressure for the case of HCO indicates that either the unconverted coal is not an effective catalyst in solvent hydrogenation reaction or HCO is not as amenable to hydrogenation as CBB. This was further confirmed when the hydrogenated HCO solvent gave only a slight increase in coal conversion during the hydrotreatment reactions. The amount of hydrogen that is consumed in the solvent hydrotreatment process can be calculated using the ideal gas equation. The number of moles of moles of hydrogen consumed is first calculated using the Ideal Gas equation using the difference in the initial and final pressures.

$$n_1 - n_2 = (P_1 - P_2)\, V / R\, T$$

The calculated number of moles of hydrogen is further used to calculate the wt% of hydrogen consumed. The weight percent of hydrogen consumed in each case is shown in Table 2. It can be seen that the wt percent of hydrogen consumed in case of CBB is much more than in HCO.

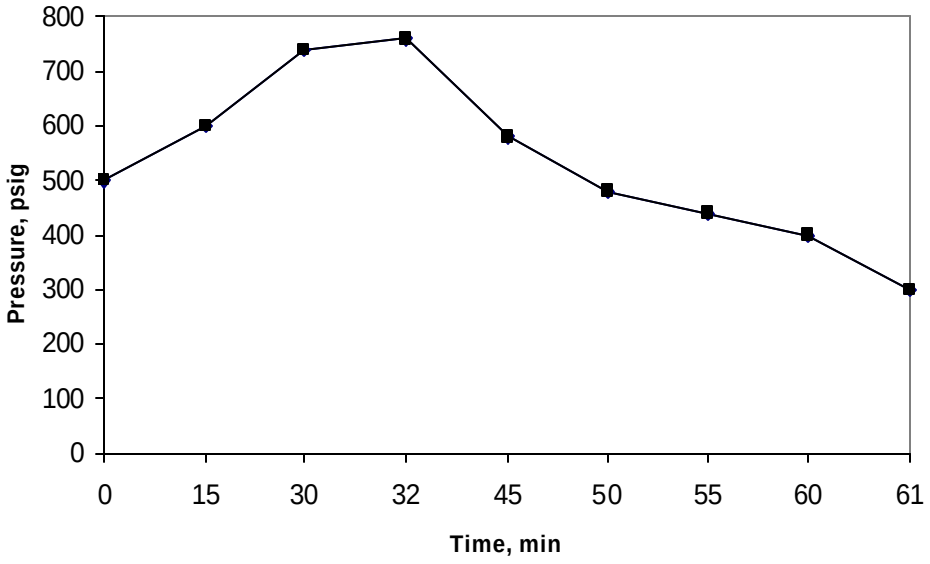


Figure 1. Pressure profile for hydrogenation of Carbon Black Base (CBB) Oil, using NiO/MoO_3 as catalyst at 500 psig H_2 (cold) and 350°C for 1 hour.

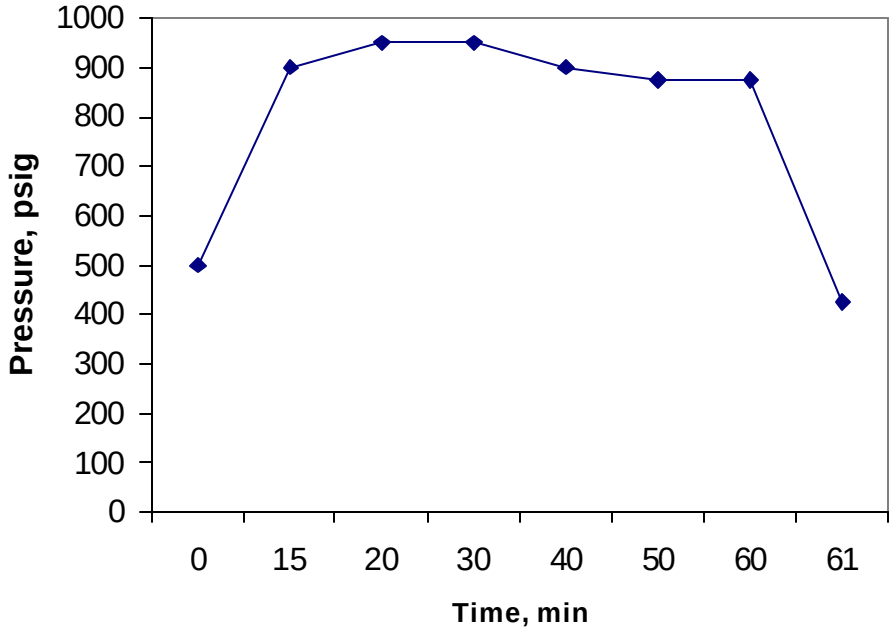


Figure 2. Pressure profile for hydrogenation of Hydrogenated Creosote Oil (HCO) using unconverted coal as catalyst at 500 psig H_2 (cold) and 400°C for 1 hour.

Table 2. Solvent Hydrogenation Conditions and Results.

Solvent	Temperature (^oC)	Pressure (psig)	Wt.% of Hydrogen consumed
HCO	400^oC	500 psig	0.0969
CBB	350^oC	500 psig	0.14

The first goal of this series of experiments was to determine the effectiveness of the two as-received coal-derived solvents HCO and CBB in the coal digestion process. For this reason, coal digestion reactions were conducted using these solvents at 400° C and 500 psig (cold) of N_2. Figure 3 shows these results. Coal alone conversion is defined as the mass of original coal (including moisture and ash) minus the mass of the residue, divided by the dry-ash-free coal mass. The coal-alone conversions for HCO and CBB are 33.75% $\pm$2.84% and 47.83% $\pm$ 2.23% respectively. The overall conversions for HCO and CBB are 88.56 $\pm$ 0.17% and 90.76% $\pm$ 0.17% respectively. The graph further shows the coal-alone and overall conversions of 68.42% $\pm$ 0.63% and 93.94% $\pm$ 0.07% respectively with pure solvent Tetralin in N_2 atmosphere. Tetralin is the model solvent for hydrotreatment reactions that gives very high conversions.

The overall conversion takes into account both the coal and the solvent. A large part of the THF solubles comes from the solvent which is completely soluble in THF. For this reason, coal-alone conversion can be taken as a more reliable measure than the overall conversion. Based on the coal-alone conversions, the figure below shows that CBB is a more effective solvent for coal digestion reactions than HCO. The result was further confirmed in a hydrogen atmosphere (500 psig) when the solvent CBB gave a much better conversion than solvent HCO.

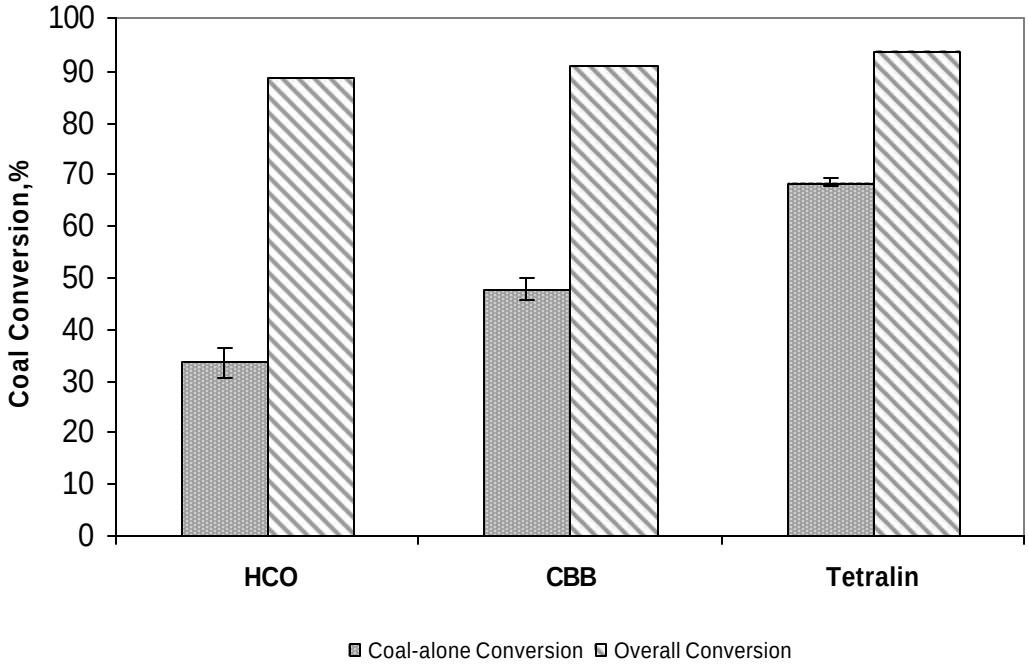


Figure 3. Percent of Coal Conversion with Neat Solvents at 400° C and 500 psig N_2 (cold).

2.1.1 Solvent Pretreatment

Figure 4 shows the conversion results of the as-received solvent HCO and the hydrogenated HCO. The solvent in this case is hydrogenated using unconverted coal as a catalyst. The coal-alone conversions for neat HCO and hydrogenated HCO (H-HCO) in N_2 atmosphere are 33.75% $\pm$ 2.84% and 38.71% $\pm$ 2.22% respectively. The conversion with Neat HCO in H_2 atmosphere is 51.75% $\pm$ 2.6% and is shown in the same graph. The results show that the conversion to THF solubles increased when the hydrogenated solvent was used. However, the conversion was much better when the neat HCO is used in the H_2 atmosphere. This shows that H-HCO is not a good hydrogen- donor solvent in the hydrotreatment of coal.

Figure 5 shows the conversion results of the hydrotreatment reaction conversion with the solvent CBB and hydrogenated CBB (H-CBB) in N_2 atmosphere. The solvent in this case is hydrogenated using NiO/MoO_3 as a catalyst. The graph further shows the conversion of CBB in H_2 for the identical reaction conditions. The coal-alone conversions for neat CBB and H-CBB in N_2 atmosphere are 47.83% $\pm$ 2.23% and 60.99% $\pm$ 0.47% respectively. The conversion for neat CBB in H_2 atmosphere was 57.22% $\pm$ 0.75%. The results in this case show that the conversion to THF solubles increased when the hydrogenated solvent is used in the presence of nitrogen. This shows that H-CBB is a very effective solvent in the coal digestion reactions

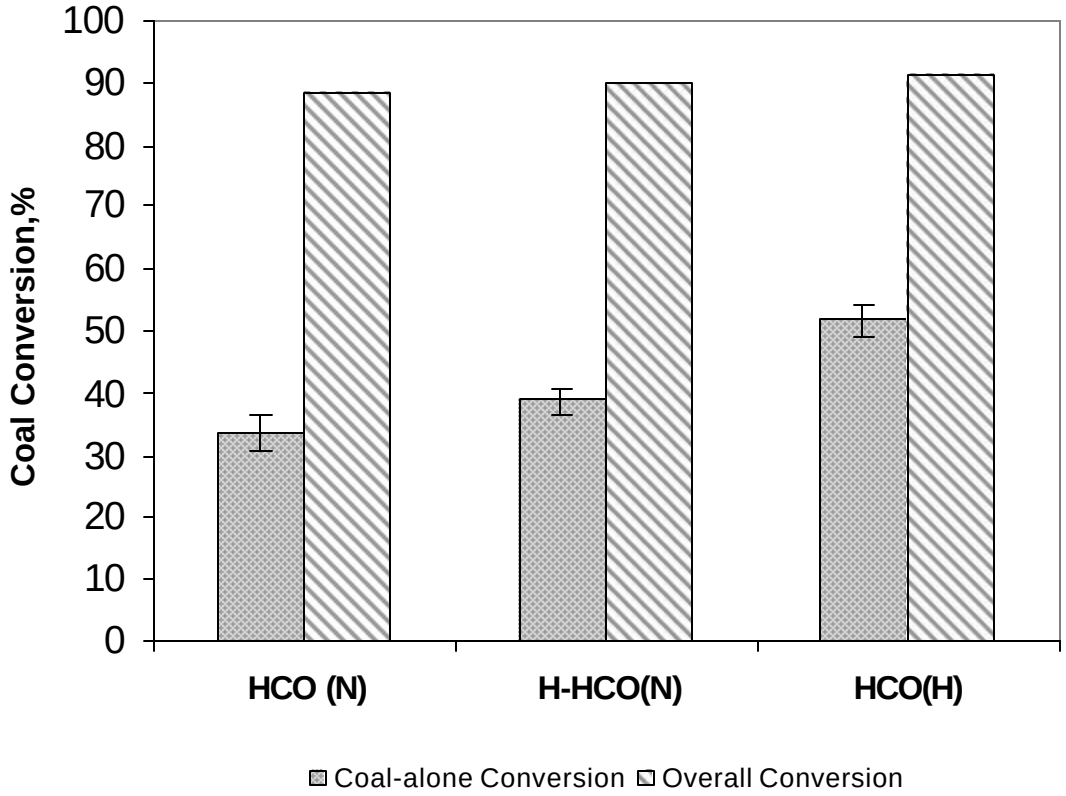


Figure 4. Percent of Coal Conversion with neat HCO and H-HCO, at 400°C and 500 psig (cold).

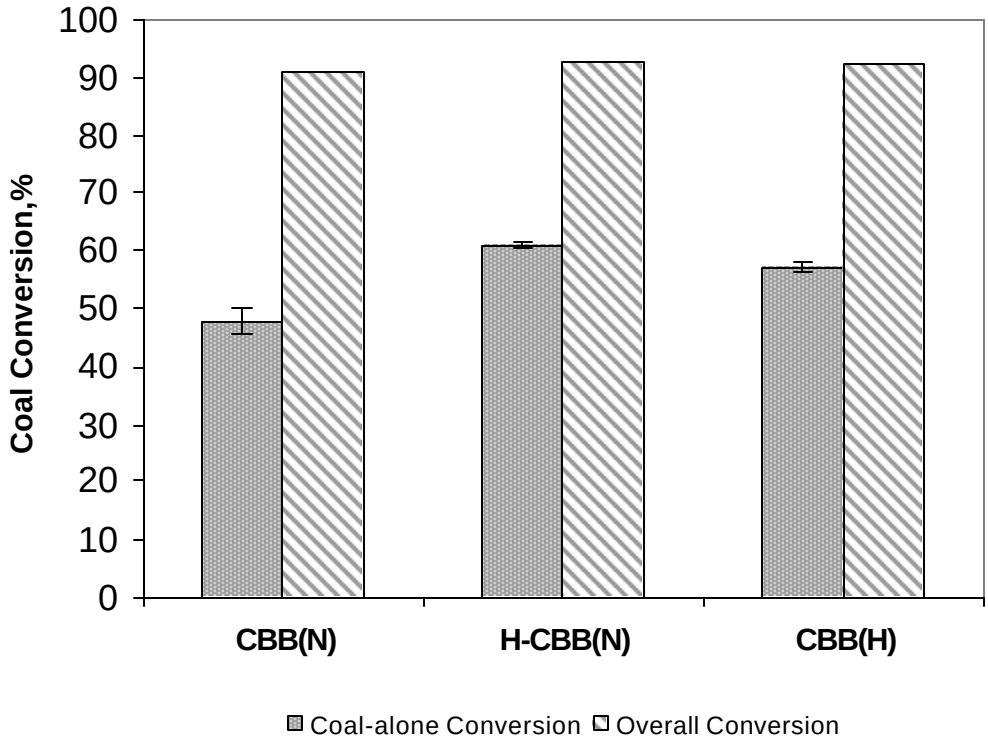


Figure 5. Percent of Coal Conversion with neat CBB and H-CBB at 400°C and 500 psig N_2 or H_2 (cold).

It can further be seen that the conversion with H-CBB in N_2 is slightly greater than the conversion with the neat CBB in hydrogen atmosphere (unlike HCO). Use of hydrogenated solvent, in this case, gives the advantage of eliminating hydrogen in the coal-reaction step of the main process. So, handling hydrogen at extreme process conditions can be avoided with an added advantage of better conversion.

2.1.2 Blends of Neat and Hydrogenated Solvents

Several reactions were performed with the blends of neat and hydrogenated solvent to determine the minimum amount of hydrogenated solvent that brings a significant increase in the conversion. Figure 6 shows the coal-alone and overall conversions of blends of neat and hydrogenated CBB for reaction in N_2. Coal-alone conversions with blends of 25%, 50%, and 75% hydrogenated solvent in raw solvent are 51.39% $\pm$ 1.26%, 52.26% $\pm$ 1.11% and 58.08% $\pm$ 1.07% respectively as shown in Figure 6. The overall conversions with blends of 25%, 50% and 75% hydrogenated solvent in raw solvent are 91.31% $\pm$ 0.48%, 91.45% $\pm$ 0.12% and 92.35% $\pm$ 0.11%. The coal-alone conversions with 25% and 50% hydrogenated CBB were found to be approximately equal and only slightly better than the conversion with the neat CBB (47.8%) and the coal-alone conversion with 75% hydrogenated solvent is only slightly less (approximately 2%) and comparable to that with 100% hydrogenated solvent.

Figure 7 shows the relationship between percent-hydrogenated CBB used in the blend and the percent coal-alone conversion to THF solubles. It was found that the addition of hydrogenated CBB increased the percent conversion, but the effect is more pronounced when the solvent contains more than 50% hydrogenated CBB.

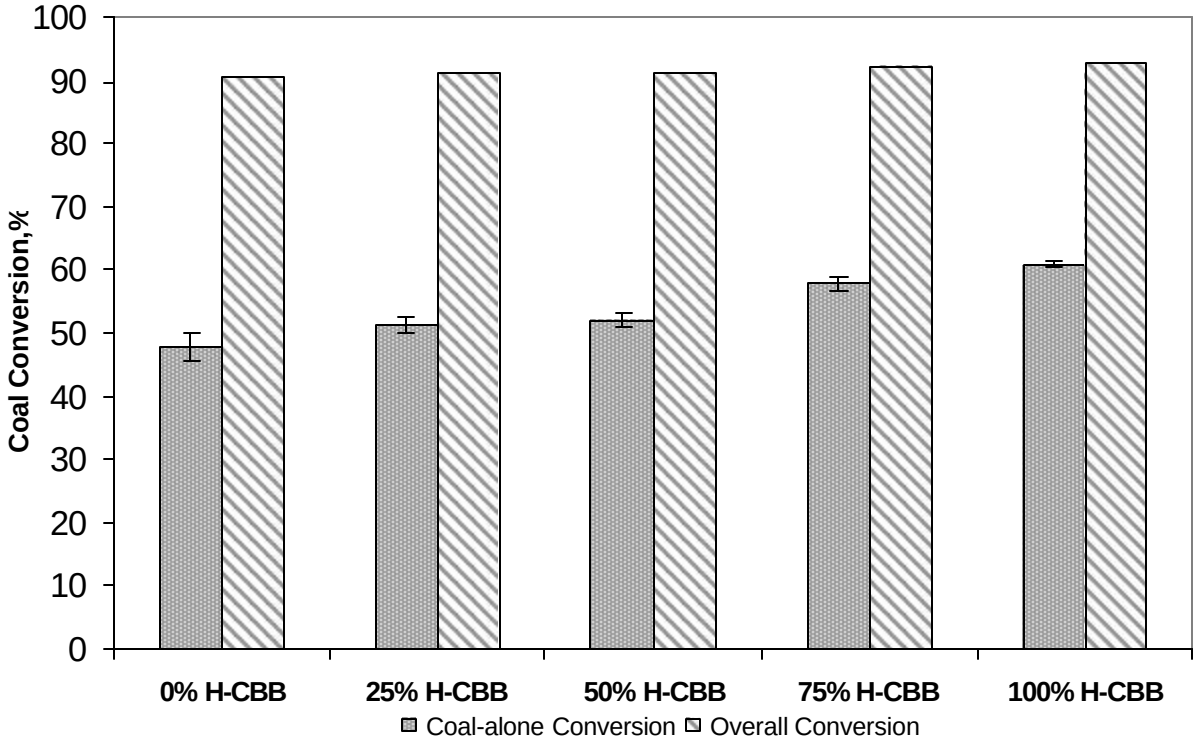


Figure 6. Percent of Coal Conversion with blends of neat CBB and H-CBB at 400°C and 500 psig N_2 (cold)

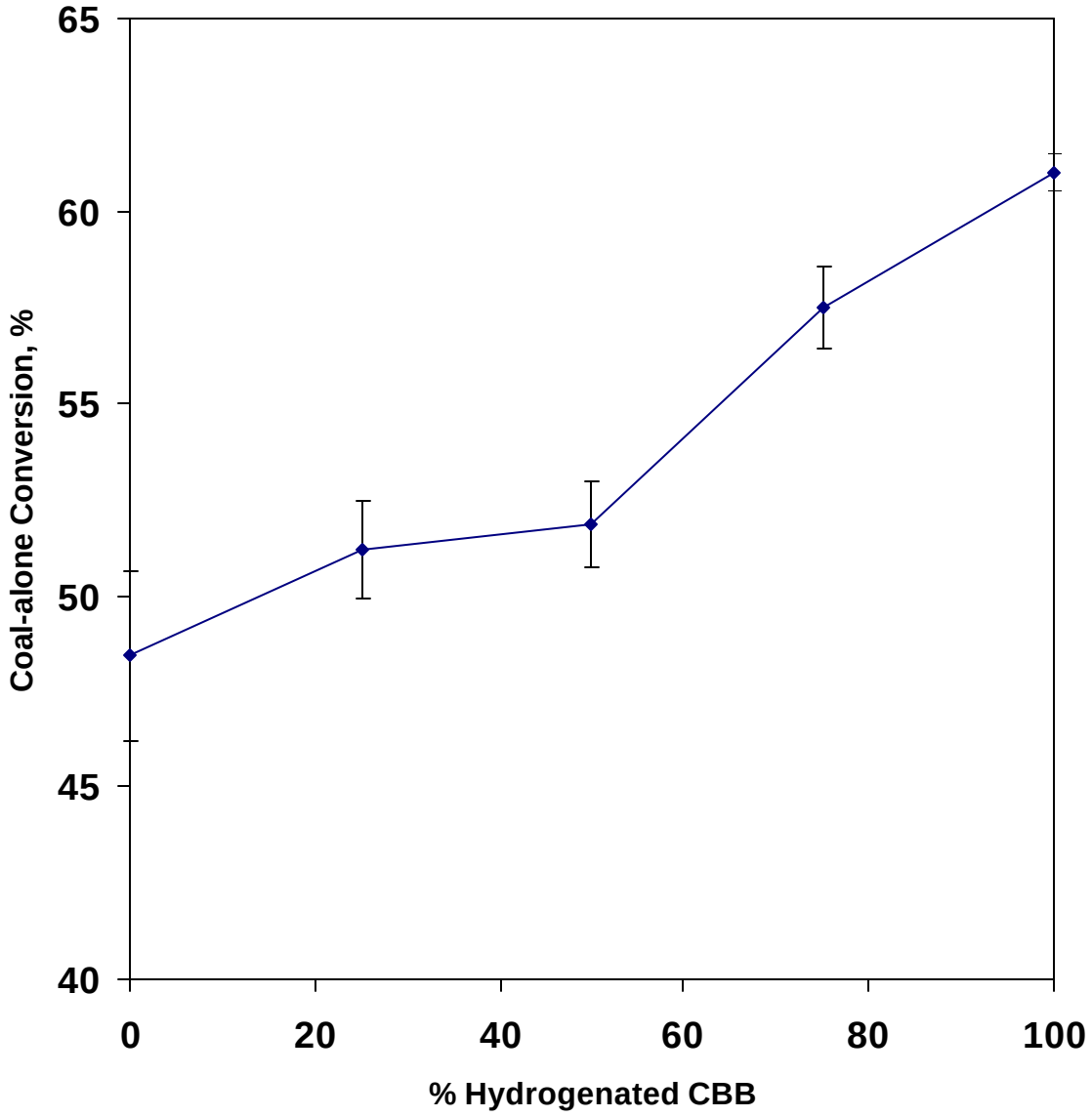


Figure 7. Relationship between percent hydrogenated CBB and percent coal-alone conversion at 400°C and 500 psig N_2 (cold).

2.1.3 Recovered Solvent and Successive Hydrotreatment reactions:

Hydrotreatment reactions were performed with the recovered solvents from the coal digestion reaction of coal with H-CBB in a N_2 atmosphere to assess their performance as hydrogen donor solvents. The coal-alone conversion with recovered H-CBB was 43.02% $\pm$ 1.56%. When we compare this value is compared with that of the neat H-CBB, it is seen that the recovered solvent does not perform as well as the neat H-CBB. Successive hydrotreatment

reactions were also run to see if the addition of neat H-CBB to the recovered brings a considerable increase in the coal-alone conversion.

Pass 1 is the reaction performed with the recovered H-CBB with the make-up neat H-CBB. Pass 2 is the reaction performed with the recovered solvent from pass 1 with neat make-up H-CBB. The blends of neat and recovered solvents used in each case are shown in Table 3. The figure below shows these results in comparison with the neat H-CBB. From Figure 8, it can be seen that the coal-alone conversions with pass 1 and pass 2 reactions were 48.74% ± 0.94% and 51.00% ± 1.27% respectively. It can be seen that the coal-alone conversion decreases with pass1 and pass 2 when compared with the neat H-CBB.

Table 3. Amount of Neat and Recovered Solvents used in the successive hydrotreatment reactions

Reaction type	Recovered solvent (%)	Neat H-CBB (%)
Pass 1	80	20
Pass 2	70	30

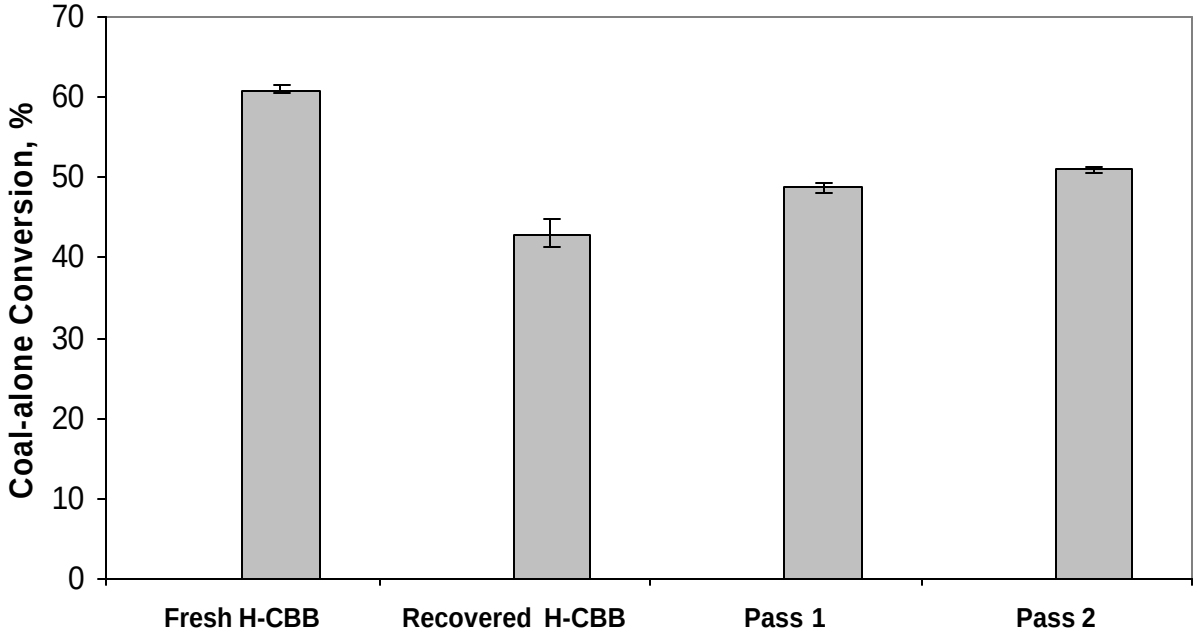


Figure 8. Percent of coal-alone conversion with recovered H- CBB and with successive hydrotreatment reactions at 400°C and 500 psig N2 (cold)

The slight increase in conversion from pass 1 to pass 2 solvent is probably due to the amount of neat make-up H-CBB used. The amount of neat make-up H-CBB used in pass 2 was increased from 20% to 30%. This is because the separation of lights (recovered solvent) becomes more difficult from recovered to pass 2. Hence, the increase in the conversion from recovered H-

CBB to pass 2 reactions can be attributed to the increase in percent of neat make-up H-CBB added.

2.2 Effect of Cover Gas

The effect of the gaseous reaction atmosphere was studied on both the solvents HCO and CBB in two different reaction atmospheres, viz. Nitrogen and Hydrogen. Figure 9 shows the coal-alone conversions of hydrotreatment reactions of coal with neat solvents HCO and CBB at 400°C and 500 psig N_2 and H_2 (cold). The coal-alone conversions for HCO and CBB in 500 psig in N_2 are 33.75% $\pm$ 2.84% and 47.83% $\pm$ 2.23% respectively. The coal-alone conversions for HCO and CBB in 500 psig H_2 are 51.75% $\pm$ 2.6% and 57.22% $\pm$ 0.75% respectively. It can be seen that the coal conversions in hydrogen are much higher than their corresponding conversion values in nitrogen for both the neat solvents. The reason for this is because of consumption of hydrogen from the gas phase and is further illustrated clearly using the hydrotreatment reaction pressure profiles.

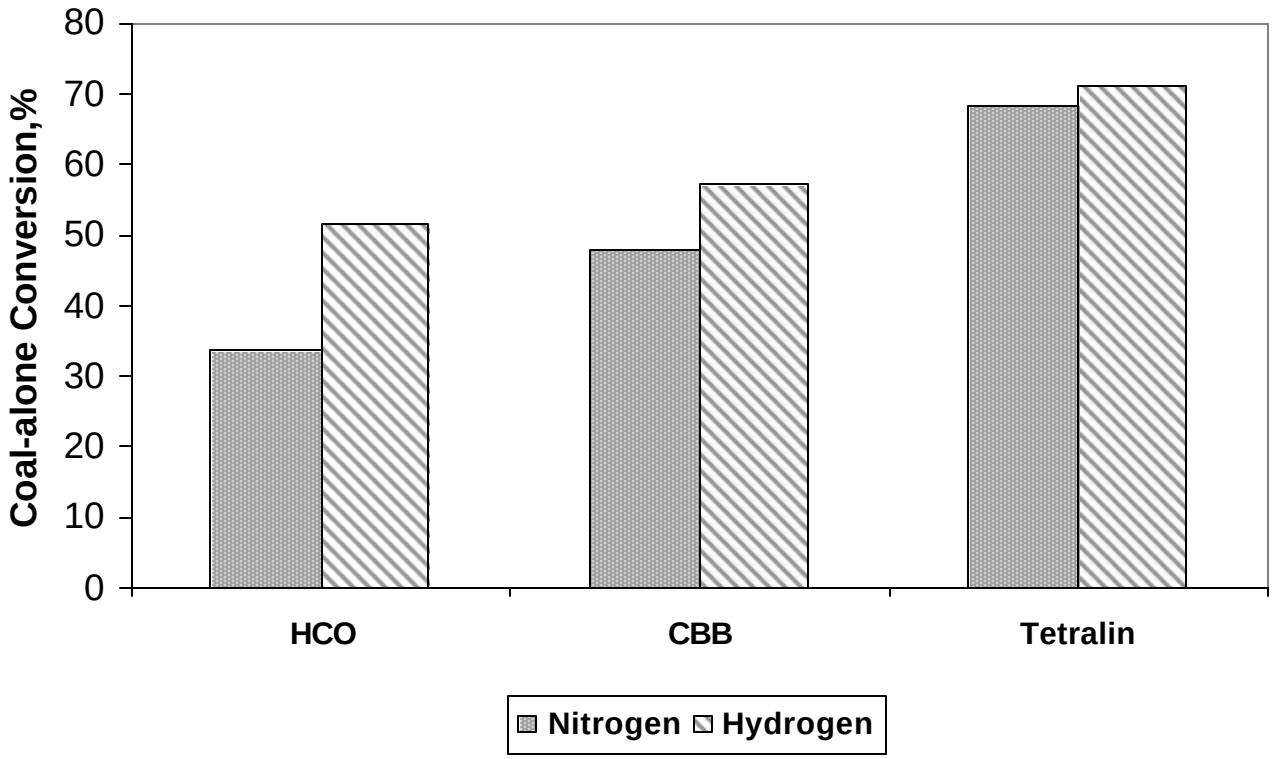


Figure 9. Percent of coal-alone conversion with neat HCO and CBB at 400°C and 500 psig N_2 or H_2 (cold).

2.3 Hydrotreatment Reactions Pressure Profiles

The study of the pressure profiles for the coal digestion reactions gives a good insight into the reaction chemistry. For this purpose, the pressure of the hydrotreatment reactions was monitored during the course of the reaction and also after quenching. Figure 10 and Figure 11 show the pressure profiles for neat solvents HCO and CBB in N_2 and H_2 atmospheres respectively. It can be seen that due to rapid heating, the pressure increases during the course of the reaction. The maximum pressure attained for both the solvents in each case did not differ greatly.

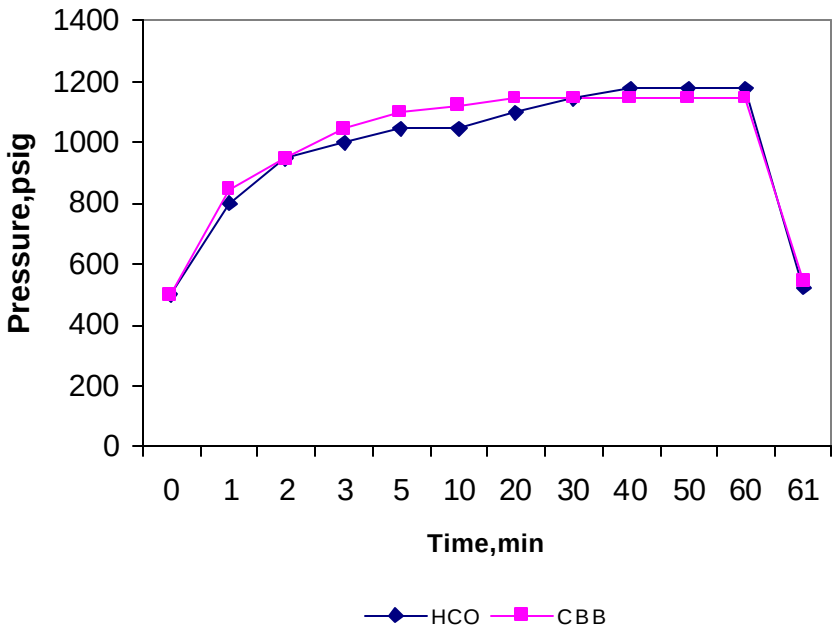


Figure 10. Pressure profile for hydrotreatment reaction with neat HCO and CBB at 400°C 500 psig N_2 (cold)

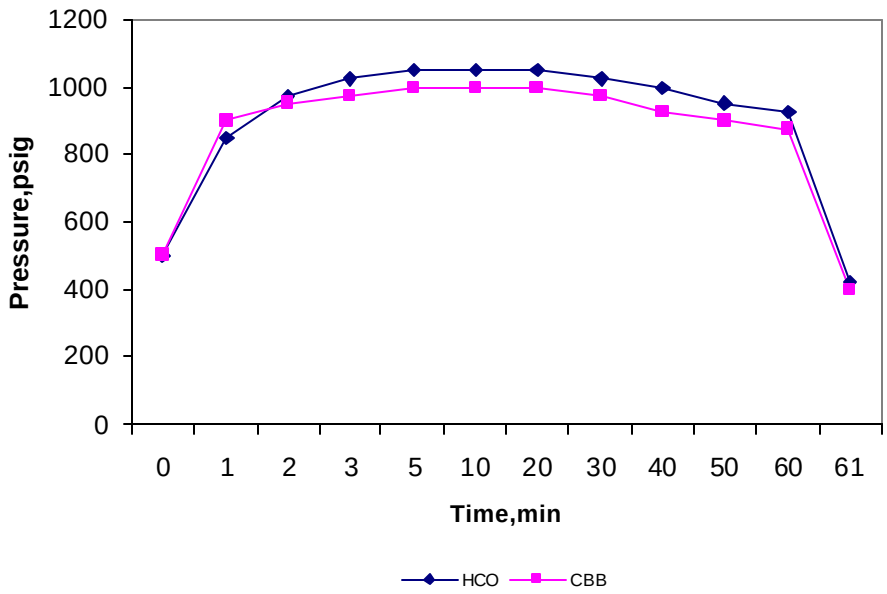


Figure 11. Pressure profile for hydrotreatment reaction with neat HCO and CBB at 400°C 500 psig H_2 (cold)

For the N_2 atmosphere, the pressure reaches a maximum value and remains at that pressure for the remainder of the reaction. In the case of the H_2 atmosphere, the pressure reaches a maximum value and then decreases with time. This shows that the hydrogen is being consumed. Also, the final cold pressure of hydrogen after quenching is less than the initial cold pressure once again indicating hydrogen consumption. This is not observed in the case of the inert atmosphere of N_2, where there will not be any gas consumption. In fact a reverse trend of an increase in the final cold pressure was observed. This additional increase in pressure accounts for the production of non-condensable product gases produced during the hydrotreatment reactions.

2.4 Effect of Reaction Temperature and Pressure

2.4.1 Reaction Temperature

The effect of the hydrotreatment, temperature was studied using the neat CBB solvent. Three different temperatures of 350°C, 400°C and 450°C were selected. Temperatures below 350°C are avoided because at these temperatures the solvent cannot accomplish a good digestion of coal. And at temperatures above 450°C, the retrogressive reactions like polymerization and reploymerization tend to dominate and a good conversion cannot be achieved.

The other reaction conditions such as solvent/ coal ratio of 5/1, pressure of 500 psig (cold) and reaction time of 1 hour were maintained the same for all the reactions.

Figure 12 shows the coal-alone conversions for neat CBB and H-CBB in N_2 atmosphere for the three chosen temperatures. The coal-alone conversions are 23.08% ± 1.73% at 350°C, 47.83% ± 2.23% at 400°C and 24.04% ± 2.7% at 450°C. This indicates that the temperatures 350°C and 450°C could not give better conversion results because of poor digestion and retrogressive reactions respectively. The same results with H-CBB show enhanced conversions but the same trend of lower conversions at 350°C and 450°C than at 400°C.

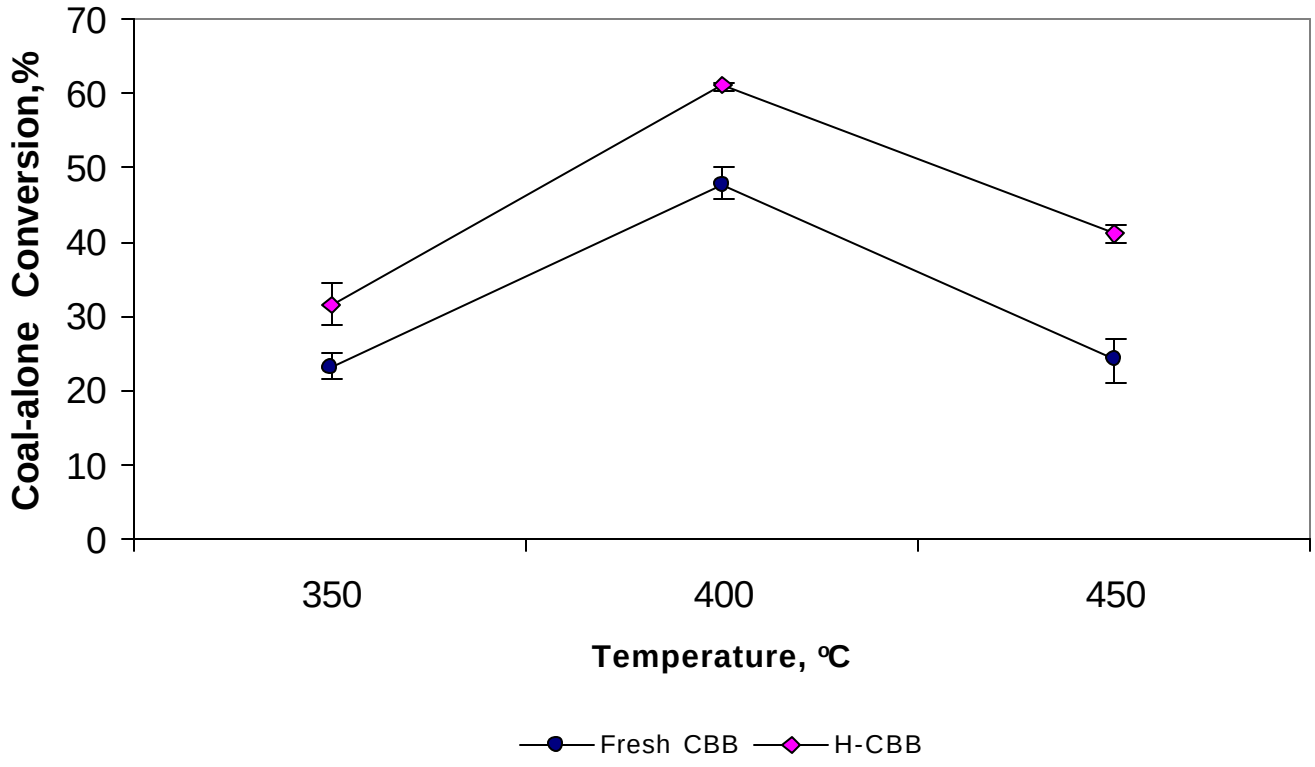


Figure 12. Percent of coal-alone conversion with neat CBB and H-CBB at different temperatures and 500 psig N_2 (cold) (Reaction time: 1 hour; Solvent/coal: 5/1)

Figure 13 shows the coal-alone conversions for CBB in H_2 atmosphere. The coal-alone conversions at 350°C, 400°C and 450°C are 25.64% ± 1.59%, 57.22% ± 0.75% and 47.21% ± 1.33% respectively. The results indicate that the presence of hydrogen gas is critical for this solvent to obtain much better conversions at 400°C and 450°C. However, the conversion did not improve much at 350°C. The conversions once again follow the same trend of poor conversions at 350°C and 450°C compared to those at 400°C. Hence 400°C appears to be the optimum temperature for the coal digestion reactions using these particular solvents.

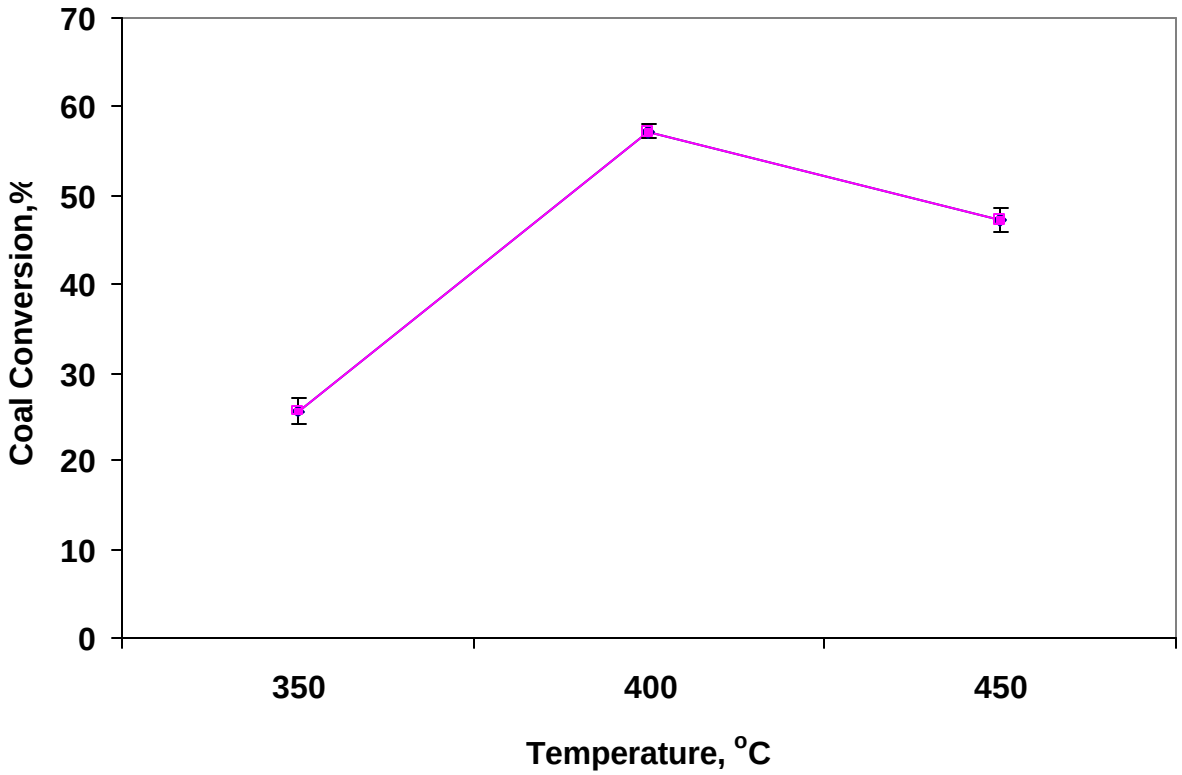


Figure 13. Percent of coal-alone conversion with neat CBB at different temperatures and 500 psig H_2 (cold) (Reaction time: 1 hour; Solvent/coal: 5/1)

2.4.2 Reaction Pressure

The pressure profiles for the hydrotreatment reactions at different temperatures in N_2 and H_2 atmospheres are shown in Figures 14 and 15 respectively. These figures show that, regardless of the reaction atmosphere, the maximum pressure attained during the reaction increases with the increase in temperature. In N_2 atmosphere, increase in temperature also resulted in an increase in the production of more non-condensibles. In the case of H_2 atmosphere, the difference between the final and initial cold pressure increases from 350°C to 400 °C and decreases from 400°C to 450°C. This is consistent with the fact of increased conversion values from 350°C to 400°C and decreased conversion values from 400°C to 450°C.

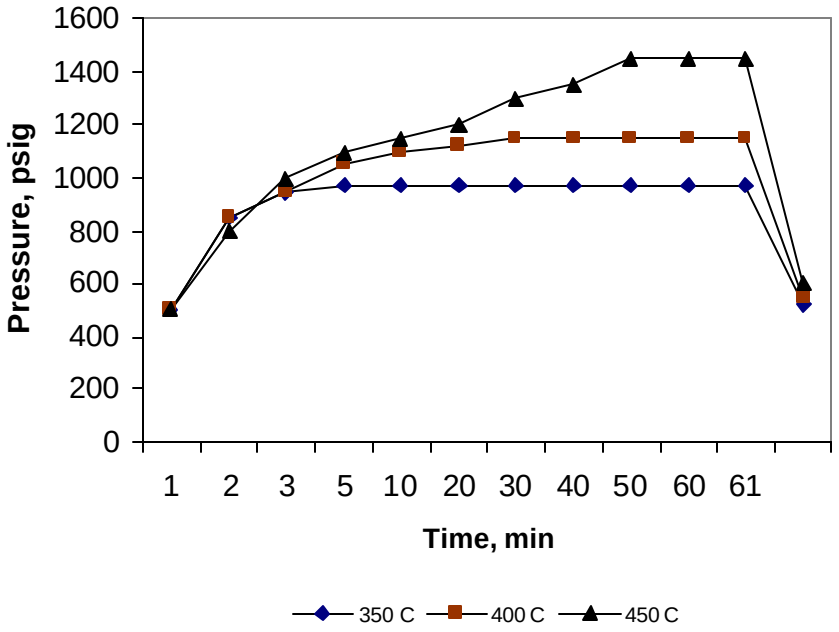


Figure 14. Pressure profile for hydrotreatment reaction with neat CBB at different temperatures and 500 psig N2 (cold)

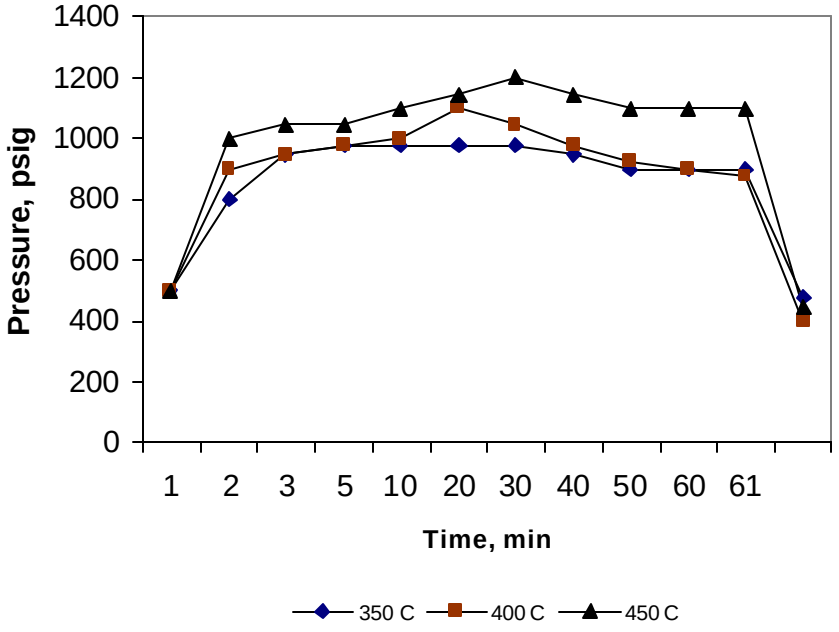


Figure 15. Pressure profile for hydrotreatment reaction with neat CBB at different temperatures and 500 psig H2 (cold)

2.5 Mass Balance

A mass balance was performed on all the coal digestion reactions to account for the losses during the process and also to check the validity of the conversion data. The amount of coal and solvent charged are noted and are considered as inputs in the mass balance calculations. The outputs include the amount of THF insolubles separated, pitch produced and the solvent recovered during the distillation. Table 4 shows the overall mass balances with neat solvents HCO and CBB at 400°C and 500 psig N_2 and H_2 (cold). The reactions were performed in duplicate and the two are shown for every reaction. It should be noted that the non-condensable gases produced during the reaction are not recovered and are not included in the mass balance. The results in all the cases show that the output is less than the corresponding input indicating losses.

The net loss of mass can occur during the reaction and/or during the product separation stages. The various reasons for mass loss could be as follows:

a. The product gases that are produced during the reaction are not recovered, but vented into the hood and hence not accounted in the mass balance. This step could account for a mass loss ranging from 2% to 5%, i.e., most of the mass loss.

b. In the filtration step, some of the solvent gets trapped in the THF insolubles. Even after several washings, there always seemed to be some amount of solvent being trapped. When the THF insolubles are vacuum dried, the solvent is vaporized and removed completely. This amount of solvent was not accounted for in the mass balance.

c. During the rotary evaporation process, some of the light components of the solvent may be condensed along with THF and separated. The mass loss in this stage is almost negligible (< 0.5%) as the solvent might not contain many low boiling components with boiling points comparable to that of THF.

d. The vacuum distillation accounts for the majority of the losses, as during the initial stages, the light components of the product mass do not condense in the collecting flask and are collected in the cold trap that is set up to protect the pump. This was further confirmed when a faintly colored solvent was found in the cold trap at the end of the distillation process. However, the amount of solvent that remains in the distillation adapters are accounted for by weighing them before and after the distillation. This amount of solvent is added to the recovered solvent.

Table 4. Overall Mass Balances of Digestion Reactions with Neat Solvents

Sol-vent	Cover Gas	Mass Coal (g)	Mass Solvent (g)	Total mass In (g)	Mass THF insol (g)	Mass Pitch (g)	Mass Recov. Solvent (g)	Total Mass Out (g)	Loss (%)
HCO	N_2	4.0013	20.01	24.0113	2.7058	2.9567	16.82	22.4825	6.80
HCO	N_2	4.0047	20.00	24.0047	2.7442	2.7812	17.01	22.5354	6.52
CBB	N_2	4.0023	20.01	24.0123	2.176	3.2960	17.07	23.206	6.52
CBB	N_2	4.0039	20.03	24.0339	2.2352	3.3574	16.93	22.5226	6.71
HCO	H_2	4.0025	20.00	24.0025	2.0769	3.3032	17.05	22.4301	7.01
HCO	H_2	4.0010	20.04	24.0410	2.1233	3.1998	17.12	22.4431	7.12
CBB	H_2	4.0041	20.02	24.02541	1.8581	3.6622	16.97	22.4903	6.82
CBB	H_2	4.0084	20.01	20.0184	1.8884	3.3420	17.20	22.426	7.08

As can be seen from Table 4, the average mass loss due to the neat solvents both in N_2 and H_2 atmospheres are almost the same ranging from 6%- 7.5%. Table 5 shows the overall mass balances for the hydrogenated solvents. The average mass losses in this case are slightly more than those with the corresponding neat solvents. This can be attributed to the fact that the hydrogenated solvents are lighter than the neat solvents and produce more light non-condensibles during the reaction, which are not recovered in the products separation.

Table 5. Overall Mass Balances of Hydrotreatment Reactions with Hydrogenated Solvents.

Solvent	Mass Coal (g)	Mass Solvent (g)	Total mass In (g)	Mass THF insol (g)	Mass Pitch (g)	Mass Recovered Solvent (g)	Total mass Out (g)	Losses (%)
H-HCO	4.0027	20.00	24.0027	2.5743	2.2631	17.34	22.1774	8.23
H-HCO	3.2002	15.10	18.3002	2.0341	1.7736	13.02	16.8277	8.75
H-CBB	4.0015	20.00	24.0015	1.8591	3.3653	16.85	22.0744	8.73
H-CBB	4.0023	20.02	24.0025	1.7279	3.0365	17.23	21.9944	9.22

Table 6 shows the overall mass balances for recovered and successive hydrotreatment reaction runs. Increased mass loss more than that for the neat H-CBB is noted in all cases. This is because of the reason that the recovered solvents are lighter than their corresponding neat solvents. Table 7 shows overall mass balances for hydrotreatment reactions with the solvents CBB and H-CBB at different temperatures (350°C and 450°C). The net mass loss with neat

solvent at 350°C in both hydrogen and nitrogen atmospheres is almost identical and comparable to those at 400°C. The increase in mass loss at 450°C can once again be attributed to the fact that more product gases are produced at higher temperatures, and these are not recovered or counted in the mass balance.

Table 6. Overall Mass Balances with Recovered Solvents and Successive Hydrotreatment Reactions.

Solvent	Mass Coal (g)	Mass Solvent (g)	Total Mass In	Mass THF insol (g)	Mass Pitch (g)	Mass Recovd Solvent (g)	Total Mass Out	Losses (%)
Recovered H-CBB	4.0002	20.00	24.0002	2.4083	3.3569	16.02	21.7852	9.23
Recovered H-CBB	4.0011	20.01	24.0111	2.3902	3.4356	16.13	21.9558	8.56
Pass 1	4.0004	20.02	24.0204	2.2018	3.5407	16.22	21.9625	9.37
Pass 1	4.0003	20.00	24.0003	2.1771	3.6451	16.03	21.8522	9.83
Pass 2	4.0022	20.02	24.0222	2.0744	4.6196	15.23	21.924	9.57
Pass 2	4.0015	20.02	24.0215	2.1252	4.6686	15.03	21.8238	10.07

Table 7. Overall Mass Balances of Digestion Reactions at Different Temperatures.

Solvent	Cover Gas	Reaction Temp (°C)	Mass Coal (g)	Mass Solvent (g)	Mass THF Insol (g)	Mass Pitch (g)	Mass Recovd Solvent (g)	Losses (%)
CBB	N_2	350°C	4.0047	20.01	3.1588	2.5575	16.85	6.23
CBB	N_2	350°C	4.0082	20.02	3.1220	2.4484	17.23	6.87
CBB	H_2	350°C	4.0050	20.02	3.0639	2.2355	16.87	8.37
CBB	H_2	350°C	4.0072	20.00	3.0410	2.0346	17.00	8.75
CBB	N_2	450°C	4.0092	20.02	3.1190	2.0615	16.82	9.22
CBB	N_2	450°C	4.0107	20.02	3.1002	2.1256	16.73	9.45
CBB	H_2	450°C	4.0040	20.02	2.2324	2.99734	16.76	9.37
CBB	H2	450°C	4.0073	20.02	2.2551	2.7519	16.83	10.03

2.6 Ash Content

Ash contents of THF insolubles and pitch fraction were determined for all the hydrotreatment reactions using ASTM D2415 method. Ash content is the inorganic oxides of the mineral matter which was present in the original coal. THF insolubles are essentially all the mineral matter present in the coal and other unconverted organic matter of the coal. So THF insolubles contain more ash than the pitch samples as most of the ash gets concentrated in the THF insolubles. Low ash content is a desirable characteristic of the pitch since the mineral matter is considered as an impurity and restricts the use of pitch as a carbon product precursor. The ash content of the neat, hydrogenated and recovered solvents was found to be negligible. Tables 8, 9, 10 and 11 show the ash contents of THF insolubles and pitches and the relative errors in their measurement.

Table 8. Ash Content of THF Insolubles and Pitches from Neat and Hydrogenated Solvents.

Solvent	Cover Gas	Ash % in THF insolubles	%Relative error	Ash % in Pitch	% Relative error
HCO	N_2	10.74	1.07	0.11	6.32
HCO	H_2	12.26	1.14	0.25	7.21
H-HCO	N_2	11.34	1.86	0.12	5.22
CBB	N_2	12.54	1.62	0.21	6.79
CBB	H_2	13.99	1.79	0.24	7.32
H-CBB	N_2	14.89	2.34	0.13	7.37

Table 9. Content of THF Insolubles and Pitches from Combinations of Neat and Hydrogenated Solvents.

Solvent	Cover Gas	Ash % in THF insolubles	%Relative error	Ash % in Pitch	% Relative error
25% H-CBB + 75% CBB	N_2	12.69	.02	0.12	7.22
50% H-CBB + 50% CBB	N_2	13.76	1.33	0.17	6.37
75% H-CBB + 25% CBB	N_2	14.92	1.472	021	7.87

Table 10. Ash Content of THF Insolubles and Pitches from Digestion Reactions.

Solvent	Cover Gas	Reaction Temperature	Ash % in THF insolubles	%Relative error	Ash % in Pitch	% Relative error
CBB	N_2	350°C	8.97	2.05	0.02	4.87
CBB	N_2	450°C	10.29	1.38	0.13	5.38
CBB	H_2	350°C	8.46	2.15	0.05	6.32
CBB	H_2	450°C	12.85	1.96	0.07	4.56
H-CBB	H_2	350°C	8.72	1.89	0.09	6.83
H-CBB	H_2	450°C	11.56	1.52	0.12	7.22

Table 11 Ash contents of THF Insolubles and Pitches with Recovered and Successive Hydrotreatment Reactions.

Solvent	Cover Gas	Ash % in THF insolubles	%Relative error	Ash % in Pitch	% Relative error
Recovered H-CBB	N_2	12.84	1.47	0.05	7.85
Pass 1	N_2	13.07	1.33	0.11	7.32
Pass 2	N_2	13.43	.1.52	0.08	6.92

These results indicate that the ash content of all the THF insoluble samples was in the range of 8-15%, and that for the pitches is in the range of 0.02-0.25%. The ash content of the THF insolubles is much more than the ash content of the pitches for each specific reaction because of the reason mentioned above. Also, the percentage relative error in determining the ash content values is less for the THF insolubles as this fraction contains most of the ash, whereas the pitches contain very little ash and hence give high relative errors in the ash determinations. Further it can be seen that the ash content of the THF insolubles is slightly higher for the reactions that give higher conversions. This is because higher conversions, indicated by the smaller amount of THF insolubles, have less unconverted coal in the residue and hence the ash in this case gets concentrated in a relatively small amount of unconverted mass.

2.7 Ash Balance

The ash values determined for the raw coal, THF insolubles and pitches are used to perform an overall ash balance on each hydrotreatment reaction. The ash balances for all the hydro-treatment reactions are shown in Table 12. The neat, hydrogenated and recovered solvents showed negligible ash contents and were not included in the calculations.

As seen earlier, mass loss is inevitable in the products separation. Due to mass loss of lighter components, the ash gets concentrated in a relatively low mass of the final pitch product during the vacuum distillation step. Hence, the calculated ash content of the pitch products is higher than the actual value and results in a positive mass balance. The positive balance is therefore a consequence of negative mass balance. For this reason, the results with the negative ash balance were discarded and not shown.

Table 12. Ash Balances of Hydrotreatment Reaction Runs.

Solvent	Cover Gas	Reaction temperature	Ash in Coal (g)	Ash Out THF insolubles (g)	Ash Out Pitch (g)	Total Ash Out (g)	(Out- in) / in (%)
HCO	N_2	400°C	0.2748	0.2892	0.0032	0.2924	6.01
HCO	H_2	400°C	0.2749	0.2779	0.0079	0.2858	3.97
H-HCO	N_2	400°C	0.2749	0.2919	0.0027	0.2946	6.68
CBB	N_2	400°C	0.2757	0.2814	0.0070	0.2884	4.61
CBB	H_2	400°C	0.2748	0.2814	0.0080	0.2898	5.31
H-CBB	N_2	400°C	0.2749	0.2768	0.0081	0.2849	3.61
25%HCBB+ 75%CBB	N_2	400°C	0.2749	0.2815	0.0032	0.2847	3.56
50%HCBB+ 50%CBB	N_2	400°C	0.2749	0.2880	0.0072	0.2952	7.02
75%HCBB+ 25%CBB	N_2	400°C	0.2749	0.2779	0.0077	0.2856	3.89
Recovered H-CBB	N_2	400°C	0.2748	0.3092	0.0016	0.3108	13.10
Pass 1	N_2	400°C	0.2748	0.2877	0.0038	0.2975	6.07
Pass 2	N_2	400°C	0.2749	0.3039	0.0029	0.3068	11.61
CBB	N_2	350°C	0.2751	0.2833	0.0010	0.2843	3.34
CBB	N_2	450°C	0.2755	0.3190	0.0026	0.3216	16.73
CBB	H_2	350°C	0.2751	0.2894	0.0011	0.2905	5.60
CBB	H_2	450°C	0.2750	0.2868	0.0021	0.2889	5.05

2.8 Coke Yield and Softening Point

Coke yield is a measure of the amount of non-volatiles present in the pitch sample. High coke yield is a desirable characteristic for the use of these pitches as carbon product precursors since the final yield of the carbon product can be maximized. The coke yield of all the pitches produced from the hydrotreatment reactions was calculated using the WVU coking method. The Softening point is the temperature at which a substance changes from a hard material to a softer and more viscous material. It is a measure of the ability of the sample to flow at a given temperature. The softening temperature gives an idea about the possible applications of the pitch material.

In the vacuum distillation step, the THF soluble fraction is separated into pitch and recovered distillate solvent. This distillation, depending upon the severity of the conditions and amount of solvent recovered affects the final coke yield and the softening temperature of the pitch. In previous work done at WVU, it was shown that the final properties of the pitch can be tailored by distilling various amounts of light distillate solvent. In the present research, in order to determine the effect of the reaction type i.e., the solvent, reaction atmosphere and reaction temperature on the final pitch material, all the distillation conditions were fixed during the distillation. The amount of solvent recovered was 80-85% and a vacuum of 30 mm Hg was maintained constant for all the distillations. The final vapor temperature was kept in the range of 200°C to 220°C. Table 13 shows the coke yield and softening temperature values of the pitch fraction for the coal digestion reactions with neat solvents in N_2 and H_2.

Table 13. Coke Yield and Softening Points of the Pitch from Coal Digestion at 400°C with Neat Solvents.

Solvent	Cover Gas	Coke Yield, %	Softening Point (°C)
HCO	N_2	54.52	154.8
CBB	N_2	57.55	145.2
HCO	H_2	61.13	157.7
CBB	H_2	45.65	122.3

The observed coke yield is comparable to the coke yield of the commercial pitches (50%-60%). The softening temperature of CBB in H_2 atmosphere is very low compared with the other solvents, hence resulting in a lower coke yield. The higher softening temperatures of above 120°C are too high for their use as the binder pitches, unless blended with lower softening temperature pitches or modified in some other way. They can be used in applications that require high softening temperature and high coke yields.

Table 14 shows the coke yield and softening temperatures of the pitch fraction for coal digestion with hydrogenated solvents in N_2 atmosphere at 400°C. The coke yields are once again in the desirable range for the binder pitches. The softening temperature of pitch with H-CBB is very high when compared with that of the solvent H-HCO.

Table 14. Properties of Pitches Resulting from Coal Digestion in 500 psig N_2 (cold) at 400°C.

Solvent	Coke Yield, %	Softening Point (°C)
H-HCO	55.06	145.5
H-CBB	68.98	171.3

Table 15 shows the coke yield and softening temperatures of the pitch fraction for coal digestion with recovered H-CBB and the successive hydrotreatment reactions with make-up H-CBB in 500 psig N_2 (cold) and 400°C. The softening temperatures were found to decrease with the use of the recovered solvent in the successive hydrotreatment reactions where additional H-CBB was included as make up.

Table 15. Properties of Pitches Resulting from Coal Digestion Using Recovered Solvents and with Successive Hydrotreatment Reactions in 500 psig N_2 (cold) at 400°C.

Solvent	Coke Yield, %	Softening Point (°C)
Recovered H-CBB	65.59	160.7
Pass 1	49.57	155.2
Pass 2	47.95	135.8

The high softening temperatures that are seen in all these cases are a consequence of the deep distillation conditions. One way of reducing the softening temperature of the pitch is by reducing the severity of the distillation as it leaves lighter species behind in the pitch. Therefore, it is important to strike a balance between the pitch yield and the softening temperature on the commercial scale.

2.9 Coke Yield vs Softening Point

Figure 16 shows the relationship between the coke yield and softening temperature of the pitches from neat, hydrogenated, recovered and successive hydrotreatment reaction solvents. In all cases coal digestion occurred at 400 ^{o}C. It can be seen from Figure 16 that there exists a linear dependence between coke yield and softening temperatures, irrespective of the solvents used and the hydrotreatment gaseous atmosphere used. A softening temperature of 140 °C correlates to a coke yield of about 50%.

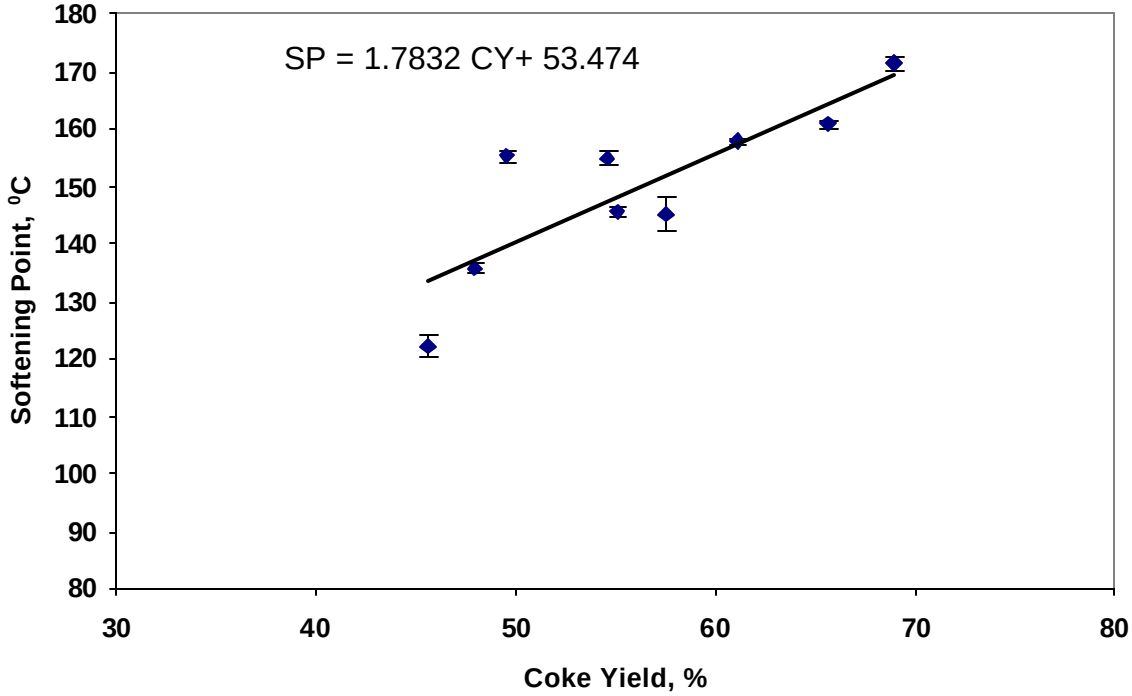


Figure 16. Relationship between coke yield and softening temperature.

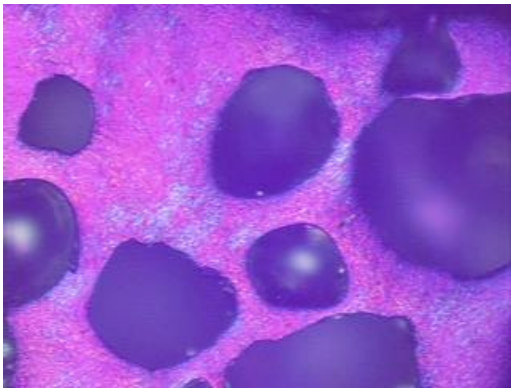
2.10 Optical Texture

Optical texture of the coke is an important property that determines its end applications. As discussed earlier, the texture can be isotropic or anisotropic. It reveals any graphitization properties of the sample. The isotropic cokes are used for production of nuclear graphite while the anisotropic cokes are used for the production of graphite electrodes. The cokes that are produced using the WVU coking method are embedded in the epoxy and polished to view them under the optical microscope. Figures 17 A and B are optical micrographs of cokes from the coal digestion with solvents HCO and CBB respectively at 500 psig N_2 (cold) and 400 °C. Figures 18 A and B are optical micrographs of cokes from the coal digestion with solvents HCO and CBB respectively at 500 psig H_2 (cold) and 400 °C.

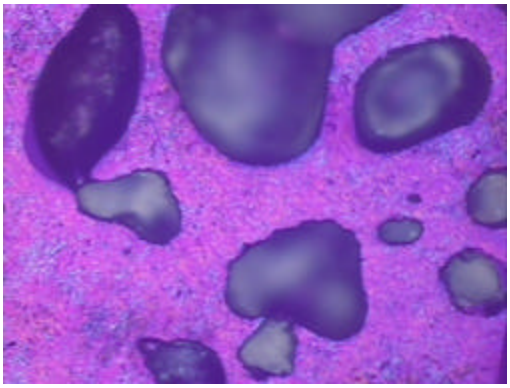
From Figures 17 and 18, it can be seen that all the cokes show an incipient mesophase indicating that they are more isotropic. Figures 19 A and B are the optical micrographs of cokes from the coal digestion with solvents H-HCO and H-CBB respectively at 500 psig N_2 (cold) and 400°C. It can be seen that the optical textures of all the coke samples are more anisotropic when compared to the cokes produced with their corresponding neat solvents. Figures 20 A, B and C are the optical micrographs of cokes from the coal digestion with solvents recovered H-CBB, pass 1 and pass 2 solvents respectively at 500 psig N_2 (cold) and 400°C. The textures of the coke produced with recovered H-CBB are isotropic and those produced with pass 1 and pass 2 solvents are more anisotropic.

Figures 21 A, B, C and D are the optical micrographs of cokes from the coal digestion with solvent CBB at 350 °C and 450 °C and 500 psig N_2/H_2. Figures 22 A and B are the optical

micrographs of cokes from the coal digestion with solvent H-CBB at 350°C and 450°C and 500 psig N_2 respectively. From Figures 21 and 22, it can be seen that, irrespective of the solvent and gaseous atmosphere of coal digestion, the coke produced from runs at a hydrotreatment temperature of 450°C are more anisotropic and those produced at hydrotreatment temperature of 350°C are isotropic. Thus it is found that higher anisotropy is produced when the hydrotreated solvents are used or the reaction temperature is higher (450°C).

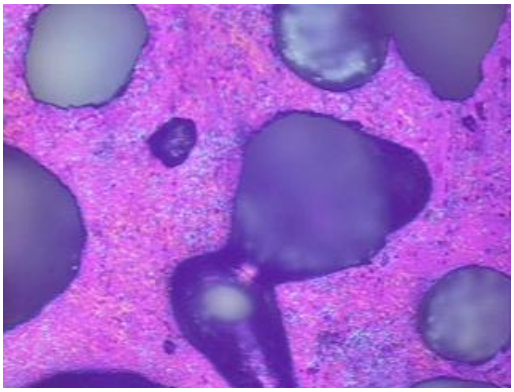


A

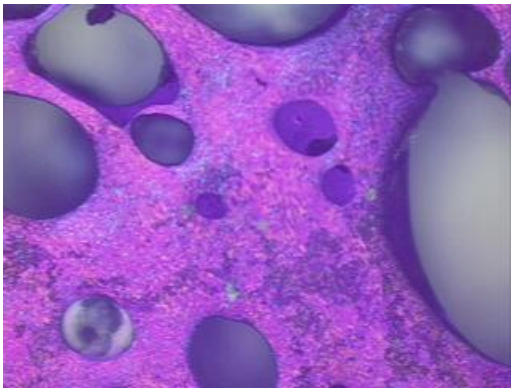


B

Figure 17. A and B Optical micrographs of cokes from the coal digestion with solvents HCO and CBB respectively at 500 psig N_2 (cold) and 400°C, 160 X, polarized light tinted plate.

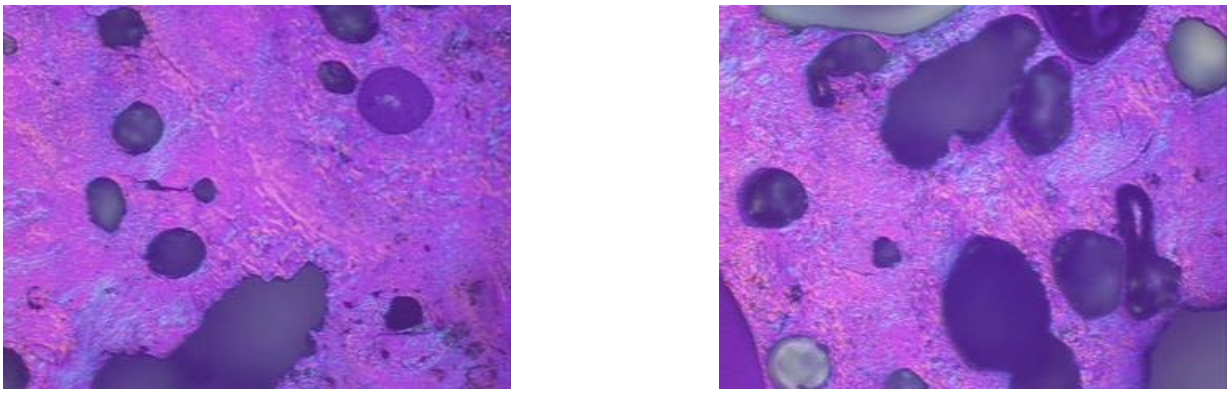


A



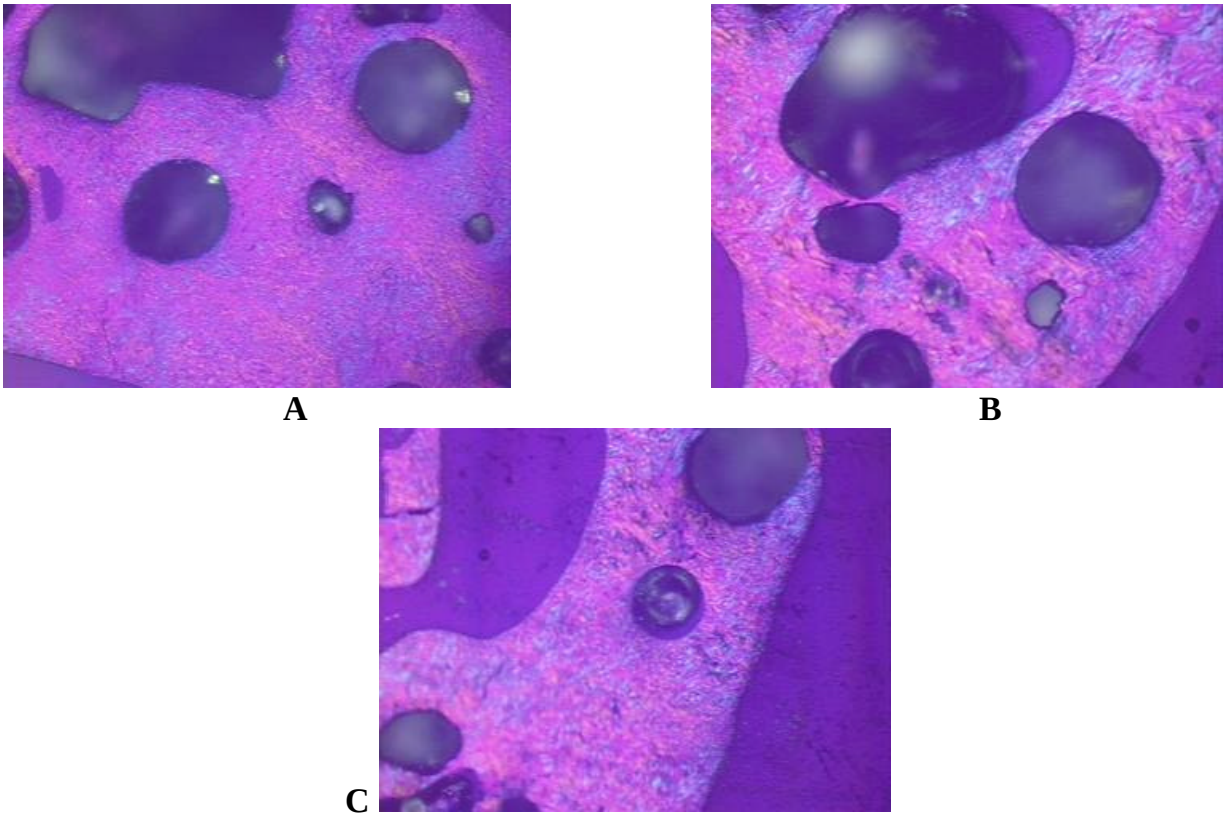
B

Figure 18. A and B Optical micrographs of cokes from the coal digestion with solvents HCO and CBB at 500 psig H_2 (cold) and 400°C, 160 X, polarized light tinted plate



A **B**

Figure 19. A and B Optical micrographs of cokes from the coal digestion with solvents H-HCO and H-CBB at 500 psig H_2 (cold) and 400°C, 160 X, polarized light tinted plate



A **B**

C

Figure 20. A, B and C Optical micrographs of cokes from the coal digestion with solvents recovered H-CBB, pass 1 and pass 2 at 500 psig H_2 (cold) and 400°C, 160 X, polarized light tinted plate.

2.11 Elemental Analysis

An elemental analysis was performed on both the input and output fractions of all the hydro-treatment reactions. The percentages of Carbon, Hydrogen, Nitrogen and Sulfur were

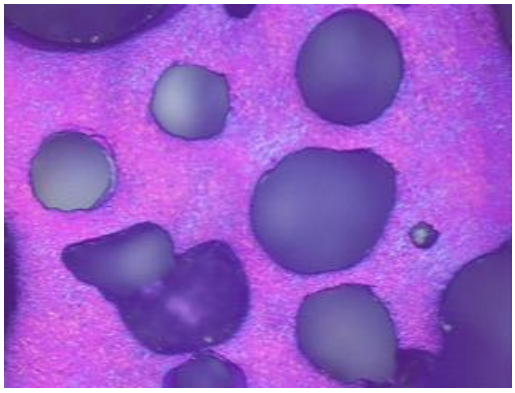
determined for all the samples. The errors in the determination of nitrogen and sulfur are much higher when compared to that of carbon and hydrogen as the former are present is smaller quantities. In some cases, a value of zero was shown for pitches due to the very minute quantities of sulfur present in those samples. Due to the above reasons, only the carbon and hydrogen amounts were considered in the further discussion. Table 16 shows the elemental compositions for neat solvent, THF insolubles, pitch and the recycle solvent with neat, as-received solvents in N_2 and H_2 atmospheres at 400°C. The following observations that can be made from Table 16 are:

a. The percentage of carbon increases from the coal (81.04%) to the pitch material.

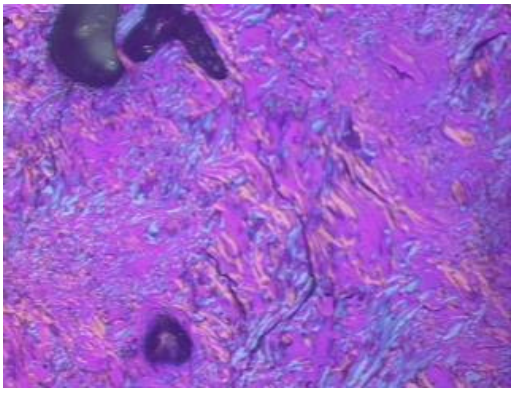
b. H/C ratio decreases from starting coal to the THF insoluble fraction indicating that THF insolubles fraction is the heavier portion of the coal.

c. H/C ratio increases from starting coal to the pitch product indicating that the pith product is the lighter portion of the coal

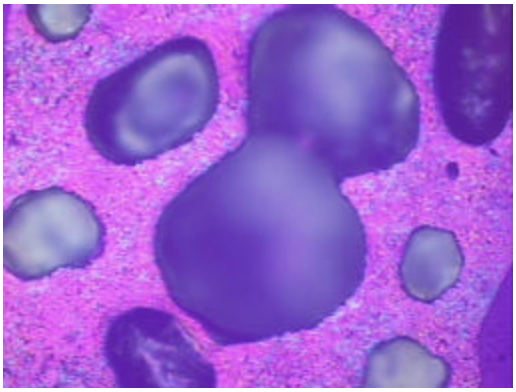
d. H/C ratio of the recycle solvent is same or slightly more than the starting solvent. This is probably because of the H-shuttling in coal transferring hydrogen from the coal matrix to the solvent or because of some associated THF that is not totally separated during the roto-evaporation.



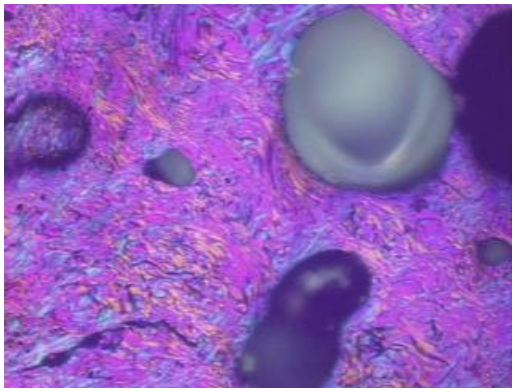
A
350°C and 500 psig N_2



B
450°C and 500 psig N_2

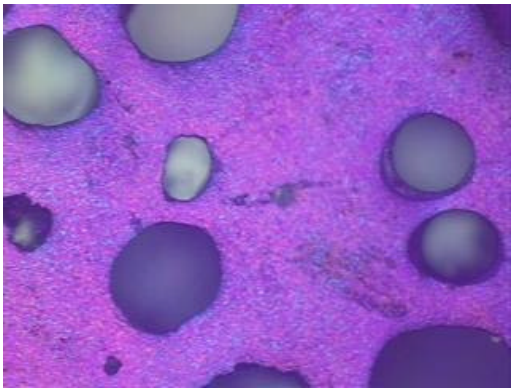


C
350°C and 500 psig H_2

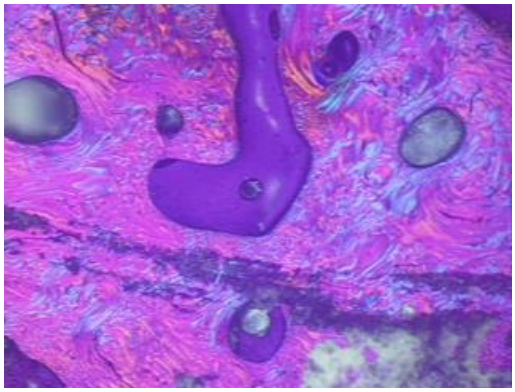


D
450°C and 500 psig H_2

Figure 21. Optical micrographs of cokes from the coal digestion with solvent CBB at 350°C and 450°C and 500 psig H_2 / N_2 (cold), 160 X, polarized light tinted plate.



A



B

Figure 22. A and B Optical micrographs of cokes from the coal digestion with solvent H-CBB at 350°C and 450°C and 500 psig N_2 (cold), 160 X, polarized light tinted plate.

Table 16. Elemental Compositions from Coal Digestion in Neat Solvents at 400°C.

SOLVENT	REACTION ATMOSPHERE	ELEMENT	NEAT SOLVENT (%)	PRODUCT FRACTION THF Insolubles (%)	Pitch (%)	Recycle Solvent (%)
HCO	N_2	C	92.3	83.7	89.3	92.6
		H	5.8	4.6	5.3	6.1
		N	2.8	1.8	2.6	1.0
		S	0.4	0.1	0.0	0.0
		H/C Atomic Ratio	0.75	0.66	0.71	0.79
CBB	N_2	C	91.6	80.4	89.7	91.1
		H	5.7	4.3	5.5	5.7
		N	1.1	2.1	2.0	1.3
		S	0.5	0.7	0.5	0.4
		H/C Atomic Ratio	0.74	0.64	0.74	0.75
HCO	H_2	C	92.3	76.6	88.9	93.1
		H	5.8	4.1	5.4	6.0
		N	2.8	1.6	3.0	1.0
		S	0.4	0.4	0.0	0.0
		H/C Atomic Ratio	0.75	0.64	0.73	0.77
CBB	H_2	C	91.6	57.5	90.2	90.6
		H	5.7	2.9	5.6	5.9
		N	1.1	1.0	1.3	1.1
		S	0.5	0.6	0.5	0.3
		H/C Atomic Ratio	0.74	0.61	0.75	0.78

Table 17 shows the elemental compositions for neat solvent, THF insolubles, pitch and the recycle solvent with hydrogenated solvents in N_2 atmosphere at 400°C. It can be seen that the H/C ratio of the recycle solvent from H-CBB is less compared to that of neat H-CBB. This explains the lower coal-alone conversions with recovered H-CBB compared to neat H-CBB solvent.

Table 17. Elemental Compositions from Coal Digestion in Neat Solvents at 400°C; Hydrogenated Solvents in N_2 Atmosphere at 400°C.

SOLVENT	ELEMENT	NEAT SOLVENT (%)	PRODUCT FRACTION THF Insolubles (%)	Pitch (%)	Recycle Solvent (%)
H-HCO	C	92.2	82.3	90.0	93.0
	H	5.9	4.5	5.6	6.2
	N	3.5	1.8	2.0	1.0
	S	0.2	0.2	0.0	0.0
	H/C Atomic Ratio	0.77	0.66	0.75	0.80
H-CBB	C	92.7	73.0	89.4	92.6
	H	6.8	3.7	5.8	5.7
	N	0.8	1.6	2.0	0.9
	S	0.0	0.7	0.4	0.5
	H/C Atomic Ratio	0.88	0.61	0.78	0.74

Table 18 shows the elemental compositions for neat solvent, THF insolubles, pitch and the recycle solvent with solvent CBB in N_2 and H_2 atmospheres at temperatures 350°C and 450°C. The H/C ratio of the pitch products did not change much from 350°C to 400°C, but decreased at 450°C both in N_2 and H_2 atmospheres.

Table 18. Elemental Compositions for Product Fractions from CBB Extractions.

REACTION TEMPERATURE	REACTION ATMOSPHERE	ELEMENT	PRODUCT FRACTION NEAT SOLVENT (%)	THF Insolubles (%)	Pitch (%)	Recycle Solvent (%)
350° C	N_2	C	91.6	77.2	90.5	93.5
		H	5.7	4.4	5.6	6.0
		N	1.1	1.7	1.8	1.2
		S	0.5	0.1	0.0	0.0
		H/C Atomic Ratio	0.74	0.68	0.74	0.77
450° C	N_2	C	91.6	86.7	91.8	93.2
		H	5.7	4.0	5.0	6.0
		N	1.1	1.8	1.7	1.1
		S	0.5	0.0	0.0	0.0
		H/C Atomic Ratio	0.74	0.55	0.65	0.77
350° C	H_2	C	91.6	79.6	90.0	92.3
		H	5.7	4.8	5.7	6.0
		N	1.1	1.6	1.7	1.0
		S	0.5	0.2	0.0	0.0
		H/C Atomic Ratio	0.74	0.72	0.76	0.78
450° C	H_2	C	91.6	75.4	91.6	92.6
		H	5.7	3.4	5.4	6.1
		N	1.1	1.7	1.7	1.0
		S	0.5	0.7	0.0	0.0
		H/C Atomic Ratio	0.74	0.54	0.71	0.79

2.12 Carbon Balance

An elemental carbon balance was performed on the hydrotreatment reactions with neat, as-received solvents in N_2 and H_2 atmospheres. These are shown in Table 19. The elemental balance was done only on the carbon as it is the major constituent of all the input and output fractions. The results were quite in agreement with their respective mass balances which showed a net mass loss. At the high hydrotreatment temperatures, carbon forms gaseous products like CO, CO_2, CH_4 etc. Most of the carbon could be lost with the gas phase products produced during the hydrotreatment reaction. Table 20 shows the elemental compositions for product fractions obtained at 400 ^oC using recovered solvent and successive hydrotreatment reactions of H-CBB.

Table 19. Elemental Carbon Balance from Digestion Reactions in N_2 and H_2 atmospheres.

Solvent	Cover Gas	Carbon In (g)	Carbon Out (g)	Losses (%)
HCO	N_2	21.7142	20.4804	5.7
HCO	H_2	21.7040	20.4010	6.0
CBB	N_2	21.5731	20.2567	6.1
CBB	H_2	21.5836	19.7465	8.5

Table 20. Elemental Compositions for Product Fractions Obtained at 400 ^{o}C Using Recovered Solvent and Successive Hydrotreatment Reactions of H-CBB.

SOLVENT	REACTION ATMOSPHERE	ELEMENT	PRODUCT FRACTION		
			THF Insolubles (%)	Pitch (%)	Recycle Solvent (%)
Recovered H-CBB	N_2	C	77.7	89.4	92.9
		H	4.0	5.9	6.1
		N	1.7	2.6	1.0
		S	0.3	0.0	0.0
		H/C Atomic Ratio	0.62	0.79	0.79
Pass 1	N_2	C	81.6	90.2	93.0291
		H	4.6	6.0	6.1649
		N	1.9	1.7	1.1872
		S	0.2	0.0	0.0000
		H/C Atomic Ratio	0.68	0.8	0.780
Pass 2	N_2	C	78.3	89.8	92.7
		H	4.4	5.7	6.3
		N	1.6	1.7	1.5
		S	0.3	0.0	0.0
		H/C Atomic Ratio	0.67	0.76	0.82

2.14 Concluding Observations

A number of parameter have been investigated to determine their importance in solvent extraction processes. The data show hydrotreated solvents are much more effective than neat solvents. Yet, recovered solvent, though not effective as the hydrogenated neat solvent, is also effective at dissolving coal to some extent.

A reliable mass balance is needed to evaluate the yield of pitch from this process. This is critically dependent upon the accuracy of the distillation process, which unfortunately was not rigorously controlled for this set of experiments.

However, an interesting feature of these experiments is that the recovered solvent appeared to be effective in dissolving coal, even without re-hydrotreating. If an accurate mass balance at larger scale can verify this trend, this implies that the solvent can be re-used many times without additional processing.

3.0 References

1. Nallani Chakravartula, Madhavi "Coal Hydrotreatment with Coal-Derived Solvents to Produce Carbon Product Precursors," West Virginia University, Master's Thesis 2005.