

PRECONVERSION TREATMENTS OF LOW-RANK COAL

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INTRODUCTION

Coal can be converted to very high yields of oil using a two-stage processing approach. To obtain even higher yields, however, it may be necessary to control the processing conditions to which coal is subjected in a manner that significantly reduces the role that repolymerization, recombination, and/or coking reactions play in the conversion process. Improvements in conversion and distillate yields may be possible if the conversion stage is subdivided into a low-severity preconversion treatment and a noncatalytic conversion step. This multistep first stage could produce a completely soluble product, theoretically increasing the effectiveness of the second-stage catalytic upgrading.

EXPERIMENTAL METHODS

A three-year program, funded by the U.S. Department of Energy under Contract Number DE-FC21-86MC10637, is underway to investigate various preconversion treatments and methods of increasing the conversion of LRCs to soluble material during the first stage. As a first step, low-severity preconversion treatments were screened to evaluate their impact on the direct liquefaction of Indian Head lignite. Several schemes were devised, and an experimental matrix was developed to screen them. Screening was carried out using the 20-cm³ microreactor system and the 1-gallon hot-charge autoclave system. Six pretreatment schemes were tested in each system. For comparative purposes, two single-step tests were performed in the microreactor system using H₂ as the reductant: one at 372°C and the other at 423°C.

Testing proceeded in two steps. The first step consisted of the preconversion treatment at the matrix-specified temperature for 60 minutes. In the case of the microreactor system, half of the microreactors were removed after preconversion treatment and the products analyzed. The remaining six duplicate microreactors were charged with hydrogen and treated at approximately 410°C for 20 minutes. When the autoclave system was used, a sample was removed for analysis following the preconversion treatment. The remaining material was then reacted with H₂ at nominally 410°C for 20 minutes. The higher than usual, first-stage temperatures were used during these studies in order to highlight the differences between the products.

RESULTS AND DISCUSSION

It should be kept in mind that, for this discussion, liquefaction is considered to be comprised of two steps: the first stage and the catalytic upgrading (second) stage. Only preconversion treatment and the first stage were studied during this work; catalytic upgrading of the products was not studied.

Microreactor Tests

Preconversion Treatment Screening Tests The conversions to THF solubles that were achieved by the six preconversion treatment schemes screened in the microreactor system are presented in Table 1. The table presents the conversions to THF-soluble material after the preconversion treatment and after the first-stage processing. Initial discussion will focus on the conversion following the first-stage processing.

The first reactant combination consisted of Indian Head lignite, A04 (coal-derived anthracene oil) solvent, and H₂. Conversions achieved with this combination after preconversion treatment and subsequent first-stage processing ranged from 37.1% at a preconversion treatment temperature of 175°C to 67.4% at a temperature of 110°C. This combination was compared with the second scheme, which consisted of lignite, A04 solvent, and CO. It was hypothesized that the nascent hydrogen produced during the water/gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H} \rightarrow \text{CO}_2 + \text{H}_2$) would be used more readily by the coal than hydrogen added as the reducing gas. Differences were noted in the conversion to THF solubles of the two schemes. These differences increased as the preconversion treatment temperature increased, so that a marked difference was noted at 250°C. At this temperature, the conversion for the A04/H₂ combination was 63.4% and the conversion for the A04/CO combination was 79.1%. The water/gas shift reaction is more active at 250°C than it is at the lower treatment temperatures. Therefore, it appears that the nascent hydrogen was more readily used by the coal than the hydrogen that was added as the reducing gas.

The third combination tested consisted of lignite, cresylic acid (CA1), and CO. This combination was chosen to determine if some of the material that physically prohibits the reaction of the coal with the hydrogen could be extracted with CA1. The results did not indicate that this was the case, as the CA1/CO scheme resulted in lower conversions at each temperature than did the A04/CO combination. For example, at 175°C the CA1/CO combination resulted in a 26.4% conversion, while the A04/CO scheme's conversion was 40.7%. At 250°C, the CA1/CO conversion was 72.1%, compared with 79.1% conversion for the A04/CO scheme.

The fourth combination made use of lignite, CA1, CO, and sodium. The use of sodium as a promoter for the addition of hydrogen to the coal structure was evaluated in this combination. A substantial increase in conversion (from 72.1% to 92.9%) was noted when sodium was present in the system at 250°C. Based upon the limited data available, it appears that sodium did promote the addition of hydrogen to the coal structure.

The fifth combination made use of lignite and tetralin in the absence of a reducing gas to determine if hydrogen transferred directly from the solvent to the coal. This approach was quite successful at the lowest preconversion treatment temperature (110°C), achieving an 87.5% conversion. A relatively low conversion of 56.4% was noted at 250°C, presumably due to the absence of CO as a reducing gas and its part in the water/gas shift reaction.

The sixth combination was performed using lignite, tetralin, and CO to determine if the hydrogen-donating solvent requires a reducing gas in order for the hydrogen transfer to take place. At 110°C, the tetralin-only system achieved an 87.5% conversion, while the tetralin/CO combination achieved a 48.8% conversion. The results were reversed at 250°C, where the tetralin/CO combination achieved a conversion of 86.3% and the conversion of the tetralin-only scheme was 56.4%. Presumably the water/gas shift reaction was a factor in the higher conversion of the tetralin/CO combination at 250°C.

Single-Step Processing Table 2 presents the conversions achieved during single-step processing using the microreactor system. The tests were performed for comparison to the first six preconversion treatment screening tests. The average conversion to THF solubles using tetralin as the solvent was approximately 90% during single-step processing at 430°C. This is slightly better than the conversion attained at a preconversion treatment temperature of 250°C for the tetralin/CO combination or that achieved by the tetralin alone at a treatment temperature of 110°C. It does not appear that the preconversion treatment had a significant impact on the conversion of lignite to THF-soluble material when tetralin was used as the solvent.

The conversion to THF solubles achieved using A04 as the solvent at a processing temperature of 430°C probably averaged near 60%, as the 76.4% conversion seems to be

out of line with the other two values. A conversion of 60% during single-step processing was somewhat less than that attained after preconversion treatment at either 110° or 250°C, but is greater than that achieved after treatment at 175°C. As was the case with tetralin, it does not appear the preconversion treatment had a significant impact on the conversion of lignite to THF-soluble material when A04 was the solvent.

When CA1 was used as the solvent during single-step processing at 430°C, the resulting conversion was approximately 45%. This value is considerably worse than that achieved by preconversion treatment at either 110° or 250°C. This seems to indicate that preconversion treatment can improve the conversion of lignite to THF-soluble material when a cresylic acid solvent is used.

Autoclave Tests

The remaining six preconversion screening tests (the seventh through twelfth combinations) were performed in the 1-gallon, hot-charge autoclave system at a nominal temperature of 175°C. The data obtained during these tests are presented in Table 3. Most of the tests were performed to investigate the addition of H₂S to the combinations of solvents and reducing gases tested in the first six (microreactor) tests. Previous studies indicated that the use of H₂S catalyzes the reactor walls. Relative to the reactor volume, the wall effects due to this catalysis are sufficient to skew the results when the testing is performed in the microreactor system. Although the use of H₂S also catalyzes the walls of the autoclave system, the effects on the products are less pronounced due to the larger volume-to-surface area ratio, resulting in a truer indication of the effects of H₂S on a given reaction.

The seventh combination tested consisted of lignite, tetralin, and argon. The resulting conversion of 78.9% was compared with that of the eighth combination, which consisted of lignite, tetralin, argon, and H₂S as a reaction promoter. The presence of H₂S resulted in a conversion of 85.3%. The use of H₂S in this instance appears to improve the conversion of lignite to soluble material.

The ninth combination tested consisted of lignite, A04, argon, and H₂S and resulted in a conversion of 80.0%. The conversion was not as high as that achieved using tetralin and H₂S. The fact that A04 is not as good a hydrogen-donating solvent as tetralin may account for the difference in conversion.

The tenth combination made use of lignite, A04, CO, and H₂S to evaluate both the reaction-promoting capabilities of H₂S in the presence of a reducing gas and the effect of H₂S on the water/gas shift reaction. The resulting conversion of 83.0% was higher than the 80.0% achieved by the A04/argon/H₂S combination. This may indicate that the presence of a reducing gas slightly improves the conversion and/or that the H₂S enhances the water/gas shift reaction.

The eleventh combination consisted of lignite, CA1, CO, and H₂S. This scheme was not especially successful when compared with the other combinations. A conversion of 70.9% was achieved, less than the 83.0% achieved using A04 solvent. This same trend was noted in the data from the microreactor tests.

The final test was the primary combination test using A04 and H₂, and it achieved the lowest conversion of all combinations tested in the autoclave system, a 60.7% conversion of coal to THF-soluble material.

Trends Noted After Preconversion Treatment Only

Conversions to THF solubles were determined for most of the tests following the preconversion treatment. These values are presented in Tables 1 and 3. When comparing the conversions after preconversion treatment only, it is possible to

discern some major differences between the reactions taking place with the different combinations.

At treatment temperatures of 175°C or less, tests performed using A04 as the solvent always had a negative conversion to soluble material of nominally -10% following preconversion treatment. In other words, at that point in the processing, the reaction had actually polymerized some of the feed slurry. In the presence of A04, upgrading of the insoluble organic matter (IOM) to soluble resid and distillable oils must take place primarily during the first stage.

Conversion to THF solubles after preconversion treatment using CA1 was positive with only one exception. This indicates that the CA1 solvent begins its conversion at very low-severity conditions, possibly through solubilization of portions of the coal.

At 250°C, the conversion to THF-soluble material was nearly as high after preconversion treatment as it was after liquefaction processing. This is most likely due to the effect of the water/gas shift reaction at this temperature. As would be expected, tests involving CO at this temperature exhibited the highest levels of conversion to THF solubles.

Comparison of Product Slates of Autoclave Tests

Evaluation of the data should not be restricted to conversion to THF-soluble materials, but should also include the product slates when possible. Due to sample size, product slates could be determined for the products of the autoclave tests only. Tables 4 and 5 present the product slates after preconversion treatment and first-stage processing, respectively. The values are presented in terms of moisture- and ash-free (maf) coal fed to the system. The product slates of the preconversion treatments will be examined first.

The tests using the light-oil solvents (tetralin and CA1) resulted in the conversion of more coal to soluble resid than the tests performed with A04 as the solvent, as shown in Table 4. The coal was probably solubilized by these solvents during the pretreatment. For the tests performed using A04, a significant portion of the coal remained as insoluble organic matter (IOM) after the preconversion treatment was completed. Table 6 presents the solvent recoveries realized during these tests. As the table shows, the solvent recoveries for the tetralin and CA1 tests were lower after the preconversion treatment than the A04 recoveries, indicating that these solvents reacted with the coal during the preconversion treatment while the A04 did not. As would be expected, the lack of gas production indicates that very little gasification took place during this pretreatment step.

Other observations can be made when the various preconversion treatment schemes are compared based upon the product slates of the first-stage processing, as given in Table 5.

An increase in CO₂ production indicated that more decarboxylation took place during the tetralin/argon test than during the tetralin/argon/H₂S test. The presence of H₂S resulted in the production of less soluble resid and IOM and more light oils and water from the coal. The H₂S seemed to aid in the conversion of the soluble resid present in the coal. During the test performed without H₂S, soluble resid equal to approximately 60 wt% of the maf coal fed to the reactor was produced at the expense of the production of light oils.

The liquid product of the A04/Ar/H₂S combination contained more IOM and soluble resid than the product of the tetralin/Ar/H₂S test. This is probably due to the heavier nature of the solvent and the reactions which took place during the preconversion treatment step.

When CO was used with the A04/H₂S combination instead of argon, more CO, CO₂, and soluble resid were produced from the coal, while less of the coal remained as IOM. The A04/CO/H₂S combination required less of the coal-derived light oils for upgrading to soluble resid than the A04/argon/H₂S scheme. However, more of the coal went to middle oil production in the presence of argon than CO. In other words, the test performed with argon resulted in the upgrading of more of the coal to lighter products than the test with CO.

When CA1 was used as the solvent instead of A04 in the CO/H₂S scheme, CO was consumed rather than produced by the coal. All of the soluble resid present in the coal as well as some of that present in the CA1 solvent after preconversion treatment were upgraded to water and light oils. This was significant when compared to the nonproduction of light oils during the test with A04. However, nearly twice as much of the coal remained as IOM at the end of the test with CA1 as at the end of the test using A04. It appears that CA1 upgrades the solubilized material better than A04, but the lighter nature of the solvent does not permit the upgrading of the heavier insoluble material.

Comparison of the A04/H₂ combination to the A04/CO/H₂S combination reveals that less gas was produced during the H₂ test. The H₂ test failed to upgrade approximately 40% of the coal, which appears in the product as IOM. Of the coal which was upgraded during the A04/H₂ test, approximately half went to soluble resid and half went to middle oils. By comparison, the majority of the upgrade during the A04/CO/H₂S test was to soluble resid with very little coal upgrading to distillable oils.

When comparing the A04/H₂ and the A04/argon/H₂S combinations, the argon/H₂S was more successful in upgrading the coal to soluble resid. Similar quantities of coal went to middle oils for both tests, but considerably more of the coal remained as IOM when treated with H₂.

CONCLUSIONS

- In the presence of A04, upgrading of IOM took place primarily during the first stage, whereas when CA1 was used as the solvent, conversion began at very low-severity conditions.
- Nascent hydrogen from the water/gas shift reaction was more readily used than hydrogen from the reducing gas.
- If any material physically prohibits conversion, it was not extractable with cresylic acid solvent.
- Sodium appeared to promote hydrogen addition to coal.
- Hydrogen-donating solvents were the most successful at converting coal to soluble material.
- The use of H₂S as a reaction promoter appeared to enhance conversion and result in generally lighter liquids than those produced when H₂S was not present.

It appears that conversion of lignite to THF-soluble material can be improved through the use of specific, solvent-dependent preconversion treatment. Small increases in conversion are possible with A04 solvent, while larger differences are possible when CA1 is the solvent of choice. This indicates that preconversion treatment can prevent some of the retrograde reactions that take place when CA1 is used as the solvent.

TABLE 1
RESULTS OF PRETREATMENT SCHEMES TESTED IN THE MICROREACTOR SYSTEM

Run Numbers	Pretreatment Temperature	Solvent	Reducing Gas ^a	Additive	% Conversion to THF Solubles	
					After Pretreatment	After 1st Stage ^b
T380, T381	110°C	A04 ^c	H ₂	-- ^d	-5.9	67.4
		A04	CO	--	-8.4	66.3
		CA1 ^e	CO	--	9.5	* ^f
		CA1	CO	Na ^g	*	63.9
		Tetralin	--	--	-9.0	87.5
		Tetralin	CO	--	*	48.8
T378, T379	175°C	A04	H ₂	--	-7.4	37.1
		A04	CO	--	-11.0	40.7
		CA1	CO	--	7.2	26.4
		CA1	CO	Na	-0.5	*
		Tetralin	--	--	-9.3	*
		Tetralin	CO	--	-9.8	*
T376, T377	250°C	A04	H ₂	--	51.5	63.4
		A04	CO	--	77.6	79.1
		CA1	CO	--	66.3	72.1
		CA1	CO	Na	74.0	92.9
		Tetralin	--	--	45.1	56.4
		Tetralin	CO	--	74.0	86.3

- ^a 1000 psi charged.
- ^b Nominal conditions of 420°C and 1000 psi H₂.
- ^c Coal-derived anthracene oil.
- ^d None used.
- ^e Cresylic acid solvent.
- ^f Samples not available for analysis.
- ^g 0.05 g NaOH dissolved in 0.05 g H₂O

TABLE 2
SINGLE-STEP LIQUEFACTION TESTS PERFORMED IN THE MICROREACTOR SYSTEM*

Run Number	Maximum Temperature	Solvent	% Conversion to THF Solubles
T372	398°C	Tetralin	78.7
		A04	69.8
		A04	73.5
T373	433°C	Tetralin	89.1
		Tetralin	91.4
		A04	57.3
		A04	61.9
		A04	76.4
		CA1	43.8
		CA1	47.4
CA1	43.0		

- * Using H₂ as the reductant.

TABLE 3
RESULTS OF PRETREATMENT SCHEMES TESTED IN THE AUTOCLAVE SYSTEM

Solvent	Reducing Gas	Additive	Run Number		% Conversion to THF Solubles	
			Pretreatment	First Stage	After Pretreatment*	After 1st Stage ^b
Tetralin	Ar	-- ^c	N459	N460	* ^d	78.9
Tetralin	Ar	H ₂ S	N457	N458	23.0	85.3
A04	Ar	H ₂ S	N455	N456	-10.6	80.0
A04	CO	H ₂ S	N463	N464	-9.2	83.0
CA1	CO	H ₂ S	N461	N462	1.8	70.9
A04	H ₂	--	N453	N454	-12.4	60.7

* At nominal conditions of 175°C and 1000 psi reducing gas.

^b At nominal conditions of 410°C and 1000 psi H₂.

^c None used.

^d Sample not available for analysis.

TABLE 4
PRODUCT SLATES OF AUTOCLAVE PRETREATMENT TEST
FOLLOWING PRETREATMENT ONLY^a

	Pretreatment Scheme				
	N457 Tet/Ar/H ₂ S	N455 A04/Ar/H ₂ S	N463 A04/CO/H ₂ S	N461 CA1/CO/H ₂ S	N453 A04/H ₂
<u>Gas</u>					
CO	0.00	0.00	-3.22	-0.12	0.00
H ₂	0.36	0.39	0.40	0.53	0.17
CO ₂	1.44	1.47	11.46	7.28	1.38
C1-C3	0.05	0.10	0.00	0.00	0.00
H ₂ S	-7.60	-0.93	-2.51	-4.07	0.00
<u>Liquid</u>					
H ₂ O	-0.68	1.55	-3.48	-1.73	-1.00
Distillable					
Oils	-69.16	-27.15	-20.77	-85.18	-37.21
Soluble Residue	96.85	12.97	8.29	84.05	24.34
Ash	1.77	1.01	0.66	1.05	-0.03
IOM	76.98	110.60	109.17	98.18	112.35

^a Values are wt% based upon 100 g MAF coal in; positive values indicate production of a component; negative values indicate consumption.

TABLE 5
 PRODUCT SLATES OF AUTOCLAVE PRETREATMENT TESTS
 FOLLOWING FIRST-STAGE PROCESSING*

	<u>Pretreatment Scheme</u>				
	<u>N457 Tet/Ar/H₂S</u>	<u>N455 A04/Ar/H₂S</u>	<u>N463 A04/CO/H₂S</u>	<u>N461 CA1/CO/H₂S</u>	<u>N453 A04/H₂</u>
<u>Gas</u>					
CO	0.71	0.50	0.37	-3.06	0.43
H ₂	-0.83	-1.99	-6.21	-1.36	-0.71
CO ₂	15.37	11.93	9.40	10.73	10.18
Cl-C3	2.32	2.17	1.49	1.71	1.45
H ₂ S	0.70	6.31	5.27	2.82	0.11
<u>Liquid</u>					
H ₂ O	4.37	8.30	0.79	8.58	-1.11
Distillable Oils	-4.34	102.50	12.23	76.51	23.15
Soluble Residue	59.70	-40.42	56.63	-29.98	27.26
Ash	-2.55	-4.05	0.06	-1.14	-0.07
IOM	24.55	14.75	19.97	29.06	39.31

* Values are wt% based upon 100 g MAF coal in; positive values indicate production of a component; negative values indicate consumption.

TABLE 6
 SOLVENT RECOVERIES OF AUTOCLAVE TESTS

<u>Pretreatment Scheme</u>	<u>Run Number</u>	<u>Solvent Recovery, wt%</u>	
		<u>After Preconversion Treatment</u>	<u>After First Stage</u>
Tet/Ar*	N459	* ^b	98.74
Tet/Ar/H ₂ S	N457	77.09	138.31
A04/Ar/H ₂ S	N455	90.84	103.07
A04/CO/H ₂ S	N463	90.43	97.24
CA1/CO/H ₂ S	N461	71.88	133.41
A04/H ₂	N453	82.54	110.99

* Tet = tetralin; Ar = argon; CA1 = cresylic acid solvent.

^b Not available for analysis.