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IMPROVING THE QUALITY OF
DETERIORATED RECYCLE SOLVENTS

DOE/PC/50784--T1

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Quarterly Report for the
Period August, 1982 - November, 1982

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Objective

The overall objective of this work is to identify reasons for solvent degeneration and to determine a feasible mechanism whereby coal-liquefaction processes can be modified to inhibit solvent degradation during the liquefaction process.

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SUMMARY

In this work, the response in product distribution (or oil yield) to different pre-treatment methods was investigated. In related past works, solvent quality was based solely on the amount of standard coal conversion. In this work, solvent quality was also determined with the use of a standard product separation procedure.

A brief discussion of related past works is followed up by a discussion of current work in the area of upgrading deteriorated recycle solvents. The effect of solvent pre-treatment on quality during thermal (non-catalytic) and catalytic liquefaction of coal was examined, and a comparison was made. In addition, the effect of the presence of typical compounds found in coal liquids (e.g. pyrene), during solvent pre-treatment, on solvent quality was also investigated.

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Introduction.

The solvent refined coal process involves the dissolution of coal in the presence of a hydrogen donor solvent at elevated temperatures (400-500 C) and high hydrogen pressures (1500-2500 psig). The solvent acts as a hydrogen shuttler between coal and hydrogen gas. It transfers chemically bound hydro-aromatic hydrogen to the coal free radicals. The solvent donor hydrogen content is replenished by the transfer of hydrogen to the solvent from the gas phase. Due to continuous recycling of the process donor solvent, it is over-hydrogenated forming saturated species. Thus, the ability of the solvent to dissolve fresh incoming coal deteriorates with an increase in the extent of recycling. This continuous deterioration of solvent is one of the major problems that need to be solved in order to enhance the economic feasibility of the coal liquefaction process.

Considerable work was done in the past by Moniz (1), at Auburn University, to explore various routes to improve the quality of depleted solvents. Recycle solvent 234, obtained from the Wilsonville SRC plant, was treated at various reaction conditions. The solvent quality was determined by two methods and the results were analyzed to determine the optimum conditions for improving solvent quality.

In the present report, the results obtained by Moniz are briefly discussed. Then, the results of some recent experimental work in the area of improving solvent quality are presented.

Past Work

The following routes were explored by Moniz for upgrading depleted solvent RS234 obtained from Wilsonville.

- Catalytic dehydrogenation of RS234 using presulfided Shell 324
- Thermal hydrotreatment of RS234 in the presence of light SRC (LSRC) and Kentucky #9 Fies coal
- Catalytic hydrotreatment of RS234 using presulfided iron oxide slurried with LSRC
- Catalytic hydrotreatment of RS234 using presulfided Shell 324 slurried with LSRC.

Experimental

A 300 cc batch magne-drive autoclave, described elsewhere (1), was used for hydrotreatment and hydrogenation purposes. The autoclave was heated over a period of one hour at an average rate of 5-7 C/min. The reactor temperature was maintained within ± 2 C of the set point. After completion of the reaction, the reactor was brought to ambient temperature within 2-3 minutes by quenching it in an ice-water bath. A gas sample was then collected for analysis. The reactor products were collected and distilled to obtain the solvent (-240 C cut).

Solvent Quality

Two test methods were used to determine solvent quality. The first, known as the kinetic test, involved using a short reaction time (10 minutes)

and an excessive solvent to coal ratio (8:1). The second, known as the equilibrium test, involved the use of a longer reaction time (30 minutes) and a lower solvent to coal ratio (2:1). The kinetic test is thought to be indicative of the rate of hydrogen transfer from the solvent to the coal, whereas the equilibrium test is thought to be indicative of the amount of hydrogen donors present in the solvent. The reaction conditions employed for both tests are shown in Table 1. The solvent quality experiments were carried out in microreactors described elsewhere (Moniz, 1982). The other parameter used for comparison of the recovered solvents was % solvent addition. This parameter is defined as the % increase in the amount of solvent having a boiling range below 240 C.

Thermal Hydrotreatment

The reaction conditions for the thermal hydrotreatment are given in Table 2. As shown in Figure 1, the solvent quality was at its maximum in the temperature range 400-420 C, then dropped off at 450 C. Since coal dissolution starts occurring only around 350 C, there was no significant increase in the solvent quality at this temperature. However, at higher temperatures, the solvent quality increased marginally ($\approx 9\%$).

Catalytic Hydrotreatment

Iron Oxide: Compared to commercial hydrogenation catalysts such as Ni-Mo and Co-Mo, iron oxide is very inexpensive. Thus, the use of presulfided iron oxide to upgrade solvent quality was investigated. Coal was excluded in these runs so that the effect of LSRC addition to the solvent could be studied separately. The results are shown in Figure 1. As can be seen from the figure, the solvent quality increased with temperature up to about 250 C (approximately

Table 1
Solvent Quality Test Conditions

Reaction Parameter	Kinetic Test	Equilibrium Test
Temperature (C)	400	400
Reaction Time (mins.)	10	30
Initial N ₂ Pressure @		
Ambient Temperature (psig)	50	50
Agitation Rate (rpm)	1000	1000
Sample Size	6 gms. solvent/ 0.75 gms. Standard Coal	5 gms. solvent/ 2.5 gms. Standard Coal

Tubing-bomb microautoclave reactor of 15 ml. volume used.

1 steel ball agitator was included to ensure mixing.

Table 2
Reaction Conditions for RS234 Solvent Pre-treatment

	Catalytic Dehydrogenation	Thermal Hydrotreatment	Catalytic Hydrotreatment Presulfided Iron Oxide	Catalytic Hydrotreatment Presulfided Shell 324
Autoclave Feed:				
RS 234, g	50	23.33	35	35
Catalyst, g	3	-----	5	5
LSRC, g	--	10.0	15	15
K9FC, g		16.67	--	--
Agitation, RPM	1500	1500	1500	1500
Reaction Time, min	90	120	120	120
Initial Pressure, psig (at ambient temp.)	100(N ₂)	1600	1600	1600
Temperature Range, °C	350-450	350-450	175-450	150-400

Figure 1. Comparison of the Thermal and Catalytic Hydrotreatment Routes used in Upgrading RS234

10% maximum improvement). Solvent quality was not significantly affected by temperature in the range 250-400 C. A further increase in the temperature reduced the solvent quality drastically. A comparison of solvent quality determined by the kinetic test and the equilibrium test is made in Figure 2. For temperatures greater than 400 C, both tests indicated a deterioration in solvent quality. The solvent quality determined by the kinetic test is consistently greater than that determined by the equilibrium test. This is most likely due to repolymerization of the free radicals from coal (the concentration of hydrogen donors could become insufficient at longer reaction times). Inclusion of catalyst and LSRC resulted in a 10% improvement in solvent quality. Some runs were conducted by adding catalyst and LSRC separately. The results indicated that both contribute equally to solvent quality improvement. When both were added simultaneously they were found to behave synergistically to yield a significant improvement in solvent quality.

Shell 324 (Ni-Mo): As shown in Figure 1, for the Nickel/Molybdenum catalyst, the solvent quality goes through a maximum and then drops off with an increase in temperature. The solvent quality increased to about 82% at 225 C. Thus, it appears that in the presence of very active catalysts, high solvent quality can be obtained with the use of relatively mild temperatures. Heteroatom removal and saturation of ring compounds causes the deterioration of solvent quality at higher temperatures.

Results and Discussion

Catalytic Dehydrogenation: Generally, the hydrogen content of recycle solvents is in the range 6.5-8.8 wt%. The solvent RS234 received from Wilsonville had a relatively high elemental hydrogen content (9.3 wt%).

Figure 2. Comparison of Kinetic and Equilibrium Solvent Qualities vs Reaction Temperature for Presulfided Iron-Oxide Hydrotreatment

Because of continuous recycling of the solvent at severe temperature conditions, saturation of aromatic rings could have taken place, resulting in an increase in hydrogen content and a decrease in solvent quality. The objective of catalytic dehydrogenation of the solvent was to upgrade it's quality by converting the saturated species to aromatics and hydroaromatics. The reaction conditions are given in Table 2. The solvent quality was found to gradually decrease from 63.8% to 55.5% with an increase in the dehydrogenation temperature from 350 to 450 C. Thus, the solvent quality for the run at 450 C was lowered by about 7% compared to the reference solvent quality of 62.5%. The following conclusions were drawn from the above work:

- Dehydrogenation of the solvent could not be carried out at high temperatures due to the formation of char and coke which reduce the hydrogen donor ability of the solvent. Catalytic dehydrogenation of the parent solvent, at the reaction conditions used here, did not increase the solvent quality.

- Evaluation of the level of upgrading achieved has been attempted by comparing the improvement in solvent quality obtained to a calibration curve prepared for a solvent such as tetrahydroquinoline (THQ) which is known to be effective.

- It was found that THQ converts approximately 95% of coal to THF solubles in a kinetic test. This conversion (or quality) is much greater than the reference solvent quality of 62.5%. Thermal hydrotreatment increased the solvent quality to 72%. The same improvement can also be achieved by adding 2% THQ to the solvent. However, 6-10% addition of THQ was necessary to yield the solvent quality obtained by catalytic hydrotreatment.

Model Compound Runs. Previous results indicated that at higher temperatures (i.e., around 375 C), the solvent quality was much lower for Shell 324 compared to that for iron-oxide. This is thought to be due to saturation of aromatic species. Thus, model compound studies such as naphthalene hydrogenation were carried out to compare the hydrogenating abilities of the two catalysts. Mild hydrogenation of naphthalene produces tetralin, a strong hydrogen donor and hence a better solvent than naphthalene. Severe hydrogenation produces decalin isomers which are very weak hydrogen donors (i.e., poor solvents). The conversion of naphthalene is represented by the following reversible equation:

A plot of mole % tetralin in the products as a function of reaction temperature is shown in Figure 3. As shown in the figure, the formation of tetralin (hydrogen-donor) occurs at a lower temperature for the Shell 324 catalyst as compared to iron oxide. The tetralin mole percent decreases very rapidly with increasing temperature due to the formation of decalins (poor-donors) for Shell 324 catalyst. These observations are in agreement with the speculative conclusions drawn from the experiments carried out to improve solvent quality. For example, it was thought that in the presence of a highly active catalyst such as Shell 324, the solvent quality deteriorates at high temperatures due to the formation of saturates.

Analytical Work: Catalytic hydrogenation is expected to increase the H/C ratio and reduce the heteroatom (N,S; etc.) content of the solvent. In this

Figure 3 Comparison of Mole % Tetralin in Products vs Reaction Temperature for Presulfided Iron-Oxide and Presulfided Shell 324 Hydrogenation of Naphthalene

work, CHN and LECO analyses were performed to determine the above changes in the treated solvent. In addition, proton nuclear magnetic resonance (NMR) spectroscopy was used to detect the changes in aromatic, hydroaromatic and saturated proton content.

The CHN analyses of the solvents obtained by the two catalytic hydro-treatment methods indicated an increase in the H/C ratio with an increase in temperature. For a typical plot of H/C ratio as a function of temperature, see Figure 4. It is worth noting that an increase in the H/C ratio did not increase the solvent quality at higher temperatures (2). This observation supports the argument that at high H/C ratios, the solvent quality decreases due to the formation of saturates.

NMR is a very useful technique to measure changes in solvent composition that would result from hydrogen transfer to the solvent during the hydro-treatment process. Based on the differences in the chemical shifts for aromatic protons, phenolic protons, olefinic protons, and the protons attached to α -, β -, or γ -carbons, the changes in the solvent composition can be determined. H_{α} represents protons on saturated carbon adjacent to H_{α} protons. The ratios, H_{α}/H_{aro} and H_{β}/H_{aro} indicate the extent of saturation of the aromatic rings.

It was very interesting to observe a correlation between these ratios and the solvent quality. For example, the solvent quality increases with an increase in the H_{α}/H_{aro} ratio for thermal as well as catalytic hydrotreatment. Similarly, at higher temperatures solvent quality decreases with a decrease in the H_{α}/H_{aro} ratio. Thus, the CHN analyses and NMR studies indicated that the decrease in solvent quality could be attributed to the formation of saturates which are poor hydrogen donors.

Figure 4 H/C Ratio vs Reaction Temperature for Catalytic Hydrotreatment of RS234

Present Work

Introduction

In the work discussed earlier in this report, solvent quality was based solely on the amount of standard coal conversion. In this work, solvent quality was also determined with the use of a standard product separation procedure. A typical procedure for product separation is shown in Figure 5. Details of this procedure are provided elsewhere (2).

Effect of Solvent Pre-treatment

The objective of this study was to investigate the response in solvent quality, to different pre-treatment methods, in terms of product distribution (or oil yield). Three solvent fractions were used. The first fraction was the baseline solvent (RS234). The other two fractions were obtained by hydro-treating RS234 in the presence of iron oxide catalyst at 350 C and 400 C. The three solvent fractions were used in coal liquefaction runs with and without Shell 324 catalyst. The results are summarized in Table 3. Section I of this table shows a comparison of product distributions for products obtained for coal liquefaction runs in the absence of catalyst. As can be seen, the use of pre-treated solvent resulted in an increase in the oils + gas fraction from 4.4 wt.% (based on MAF coal) for the base-line solvent run, to 12.5 wt.% for the run using the solvent which was pretreated with iron-oxide at 350 C and 11.3 wt.% for the run using the solvent which was pretreated at 400 C.

The use of Shell 324 catalyst resulted in a significant increase in the oil fractions (or, indirectly, solvent quality). The effect of solvent

FIGURE 5 BLOCK DIAGRAM FOR PRODUCT SEPARATION PROCEDURE

Table 3

Response In Product Distributions to Different Solvent Pretreatment Methods

I				II		
Solvent Code	RS 234	I05	I07	RS234	I05	I07
Catalyst (g)				1.0	1.0	1.0
Oils + Gas (wt.%)	4.4	12.5	11.3	44.1	46.8	46.5
Asphaltenes (wt.%)	45.5	42.5	39.3	10.6	8.3	9.8
Preasphaltenes (wt.%)	15.4	14.0	16.6	2.0	2.5	3.0
IOM (wt.%)	34.7	30.9	32.9	43.4	42.4	40.8

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I: Thermal Liquefaction (1250 psig H₂ pressure; no catalyst)II: Catalytic Liquefaction (1250 psig H₂ pressure; 1g Shell 324 catalyst)

RS234: Base-line solvent

I05: Base-line solvent hydrotreated with iron oxide catalyst at 350C for 2 hrs.

I07: Base-line solvent hydrotreated with iron oxide catalyst at 400C for 2 hrs.

Reaction Conditions:

Solvent = 4 g

Coal = 2g

Temperature = 425C

Time = 1 hr

Agitation Rate = 850 rpm

Initial H₂ Pressure (at 25C) = 1250 psig

pretreatment was not as pronounced in the catalytic liquefaction run as in the non-catalytic liquefaction runs.

Since pyrene, which has a four ring structure, is typically found in coal liquids it was decided to examine the effect of its incorporation in the solvent on product distribution (or oil yield). The reaction conditions for the pyrene treatment, and the product distribution results, are given in Table 4. Results shown in the table indicate that in the catalytic as well as non-catalytic runs there is an increase in oil yield due to the addition of pyrene (from comparison with Table 3). However, further investigations are needed to ascertain that pyrene treatment enhances solvent quality.

In the previous work, for the iron oxide treated solvent, it was observed that the changes in solvent properties had a greater effect on the kinetic test than on the equilibrium test. The following work was carried out, to determine if the same is true for Shell 324 treated solvent. Before determining the equilibrium quality of the solvent, the uniformity of the procedures used by different personnel was ensured by checking the reproducibility of some data points given by Moniz (1). The reproducibility was within 5-10%. The equilibrium solvent quality values for Shell 324 treated catalyst as a function of temperature, are given in Table 5. As shown in the table, the solvent quality was maximum (65.22%) at 350 C. Similar results were also obtained by Moniz (1) for the iron oxide treated solvent. Thus, there was good agreement between the results obtained by the two investigators. No significant effect of the catalyst type on equilibrium solvent quality was observed. For example, at different temperatures, the solvent quality was in the range 58-68% for the iron oxide hydrotreated solvent. For the Shell 324 treated solvent, the range was 55-65%.

Table 4
Response In Product Distribution to Pre-treatment
of Solvent With Pyrene

Catalyst	--	1g
Gas	1.3	0.4
Oil	9.5	59.4
Asphaltenes	45.0	10.1
Preasphaltenes	14.0	1.1
IOM	30.4	29.0

Treatment Conditions

Solvent (RS234) = 35g
 Pyrene = 5g
 Catalyst (Shell 324) = 5g
 Temperature = 250°C
 Time = 2 hrs.
 Agitation = 700 rpm
 Pressure, H₂ = 1250 psig (initial

Table 5
Results of Equilibrium Test Using Catalytic Hydrotreatment
of RS234 with Presulfided Shell 324 Slurried with LSRC

Solvent	Reaction Temperature, °C	% Solvent Quality
NM1	150	55.50*
NM2	200	59.27*
NM3	250	62.50*
NM4	300	64.57
NM5	350	65.22*
NM6	375	63.34
NM7	400	61.27

* Average of duplicate runs

Conclusions

The following conclusions can be drawn from the above work:

- Low-temperature, catalytic hydrotreatment of deteriorated process solvents was found to have a significant effect on solvent quality during thermal (non-catalytic) liquefaction of coal. However, solvent pretreatment was found to have no significant effect on solvent quality during the catalytic liquefaction of coal.
- Low temperature, catalytic hydrotreatment of deteriorated process solvents in the presence of compounds typically present in coal (e.g. pyrene) appears to have good potential for enhancing solvent quality during coal liquefaction.
- The effect of temperature on equilibrium solvent quality appears to be independent of the type of catalyst with which the solvent is pretreated.

References

1. Moniz, M. J., M. S. Thesis, Auburn University, 1982.
2. Brooks, D. C., M. S. Thesis, Auburn University, 1982.