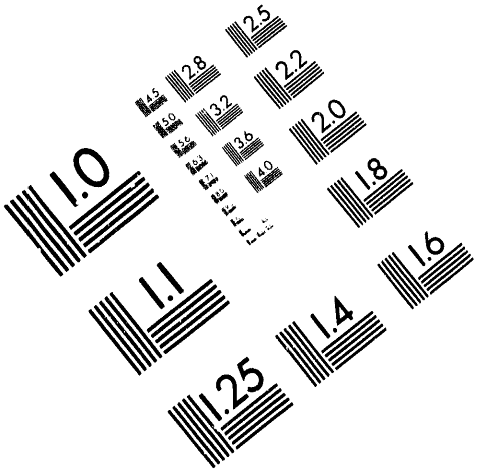

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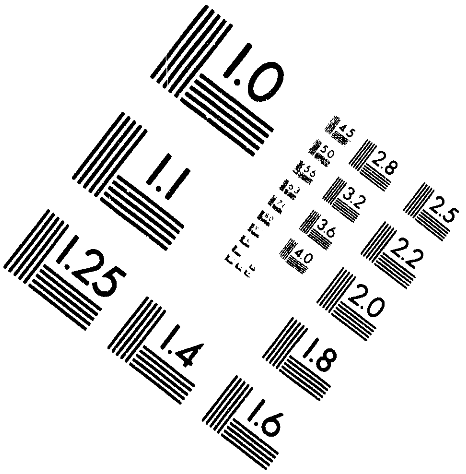

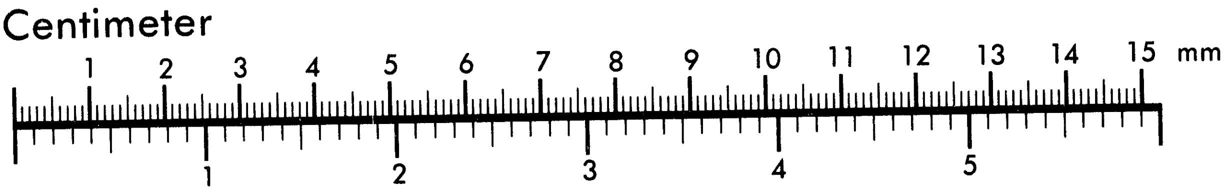

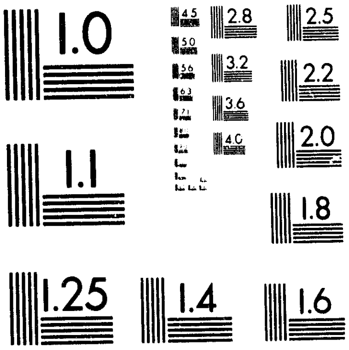

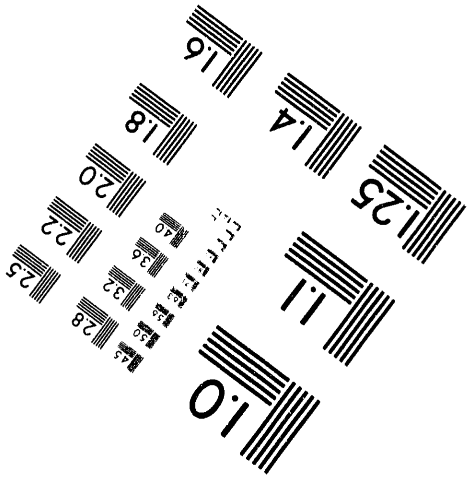

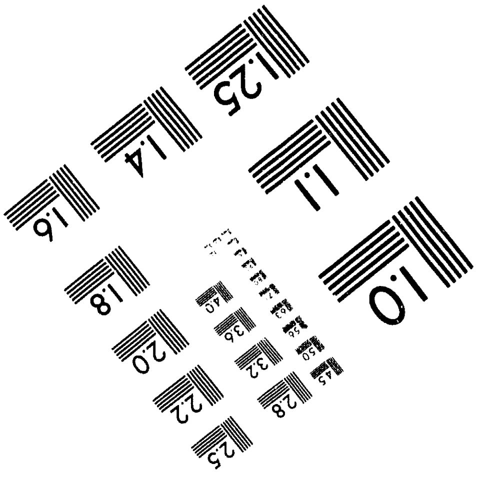

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SRI International

Quarterly Report No. 9 - 15 February 1994

HIGHLY DISPERSED CATALYSTS FOR COAL LIQUEFACTION

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SUMMARY

The objectives of this project are to study the effect of pretreatment methods on the two-stage liquefaction process. In particular, the effects of dispersed catalysts and carbon monoxide atmospheres on a coal liquefaction process. The project is divided into three technical tasks. Task 1 and 2 deal with the analyses and liquefaction experiments, respectively, whereas Task 3 deals with the economic impact of utilizing the pretreatment methods. This quarter we concentrated on Tasks 1 and 2, which are summarized below.

Task 1. Analytic Support

This task is in support of Task 2, and involves the analyses of the liquefaction products and catalysts involved in the liquefaction runs. This quarter we analyzed two sets of liquefaction experiments, one involved the liquefaction of Black Thunder Coal with the corresponding recycle vehicle, and the second set of liquefaction runs involved the liquefaction of Argonne North Dakota Lignite.

Task 2. Laboratory Scale Operation

During this quarter we compared coal conversions of Black Thunder coal and recycle solvent using $Fe(CO)_5$ and carbon monoxide/hydrogen atmospheres and a MolyVanL molybdenum catalyst under a hydrogen atmosphere. We also continued our investigation of the effect of water on the conversions. In the past quarter we found that addition of water seemed to decrease the amount of oils; this quarter we determined the effect of water with the recycle solvent alone, (no coal added) under similar conditions, and again produced a decrease in oil yields. FIMS analyses of the hexane and toluene soluble fractions seem to indicate that in the experiment when water was added, a considerable amount of light material remained behind in the toluene layer, suggesting that somehow the addition of water decreased the amount of extracted material, perhaps by increasing the amount of polarity of the product.

When the conversion was conducted with the MolyVanL molybdenum catalyst a good quality product in terms of lower viscosity was produced; however, conversions to THF soluble material was not increased. We believe the molybdenum catalyst hydrogenated the recycle vehicle rather than effectively converted the coal. In order to eliminate the effect of solvent we have often

conducted experiments in an inert solvent with Argonne coals. During this quarter we conducted several coal conversions experiments using an Argonne North Dakota lignite. We compared several dispersed Fe catalysts and in addition, a nickel catalyst. We investigated nickel as a catalyst since we believe this metal may be more effective in decarboxylating low rank coals. Consistent with this premise we found that the nickel catalyst gave the highest conversions.

INTRODUCTION

Integrated processes to liquefy coal have evolved to the current two-stage close coupled catalytic configurations now being used at Wilsonville.[1-4] Recent estimates (1990) indicate that two-stage conversion of coal to liquids has a product cost in the area of $38 per barrel and the improved quality of the liquids makes them equivalent to oil costing $33 per barrel. Several areas in the conversion technology have been identified that, if improved, should make coal converted to oil more cost competitive with petroleum products. These areas include pretreatment and cleaning methods, choice of feedstock, novel catalysts, and processes to improve hydrocarbon recovery. The objective of this project is to address possible methods of improving the efficiency of these and other steps in the integrated process so that the overall conversion will show increased cost effectiveness. This work will concentrate on individual steps and technoeconomic evaluations to provide information on their relative effectiveness toward the overall goal of $25 per barrel.

So far, most work at Wilsonville has involved bituminous coals, which are much easier to convert than lower-rank coals such as Wyodak and lignites.[5] The lower-rank coals are more abundant and cheaper, and conversions lead to a higher quality product with less heteroatom content.[6] However, the yield of liquid products is low. The low conversion of these coals has been attributed to their high oxygen content, and the carboxyl groups are thought to cause retrograde reactions by free radical processes.[7,8] Additionally, phenolics often are associated with retrograde reactions leading to polymeric furans.[9,10] Developing a process for utilizing these coals in high conversions would greatly improve the economics of coal conversion. Several approaches, including highly dispersed catalysts and coal pretreatment techniques, have been suggested to overcome these detrimental reactions. In recent work we have studied both of these approaches to enhance the convertibility of coal and minimize the retrogressive reactions.

This project is designed to evaluate the feasibility of using low-rank coals such as Wyodak and lignite in a two-stage liquefaction pilot demonstration unit (PDU). The primary objectives are to (1) synthesize and impregnate coal with high activity, highly dispersed catalysts (dispersed on the molecular scale); (2) develop an understanding of these catalysts in terms of their reactivities toward hydrogenation and hydrogenolysis, especially in terms of removing phenolics and carboxylates, which are thought to cause most retrogressive reactions; (3) monitor the activities and physical properties of these catalysts during coal liquefaction processes and compare them with those of other types of catalysts; and (4) evaluate process cost improvements that might be realized through the use of low-rank coals, dispersed catalysts, and CO/H_2 for coal liquefaction in a two-stage close coupled configuration.

TASK 1: ANALYTICAL SUPPORT

The objectives of this task are to provide analytic support for the laboratory conversion studies conducted in Task 2. During this quarter the fractionated products from the coal liquefaction experiments and for C, H, and N content, and in selected cases, the oxygen content. The gas analysis of the coal liquefaction products was also analyzed to determine differences in light gases as a function of catalyst and process conditions.

Elemental Analyses

This quarter we analyzed products from two types of coal conversions. One was the Black Thunder conversions using the corresponding recycle vehicle, as described in previous reports, and the second was conversions of an Argonne North Dakota lignite in an inert non-donor solvent. The purpose of the later type of conversions are to better study the specific effect of the catalyst without the interferences of solvent. We chose the lignite so that we can compare these conversions with those in our earlier work.

As described in Quarterly Report 8, the conversion products from the Black Thunder coal and recycle vehicle were separated into the following fractions: THF-insoluble, THF-soluble/toluene-insoluble, referred to as preasphaltenes, toluene-soluble/hexane-insoluble fractions, referred to as asphaltenes, and hexane solubles, referred to as oils. The Argonne samples, in contrast, were simply separated into toluene-soluble and toluene-insoluble fractions.

Table 1 lists analyses of the product slate for conversions of the Black Thunder coal and recycle solvent catalyzed by iron carbonyl as well as reactions catalyzed by MolyVanL. As shown by the elemental analyses for the iron carbonyl reactions, the reactions involving CO atmospheres appeared to give slightly higher H/C ratios for the asphaltenes and oils. Likewise, the molybdenum catalyzed conversions also gave slightly higher H/C ratios. As discussed last quarter, the analyses of the oils required encapsulation in DSC pans due to volatility, so the analyses may be more subject to error due to entrapped air or leaks. We also submitted selected products for direct oxygen analyses and found that the iron catalyst in the presence of carbon monoxide appears to remove oxygen. For instance, for the $Fe(CO)_5$ and H_2 reaction, the oxygen content of the asphaltene and oil fractions were 4.78% and 2.37% respectively. For the reactions conducted in the presence of 50% CO the oxygen contents were 2.74% and 1.74% respectively, and when water was present during the reaction in the 50% CO run, the oxygen contents were similarly low at 2.68% and 1.76%, respectively. Interestingly, these values were quite similar to those of found for the molybdenum catalyzed conversion (2.9% and 1.83% for the corresponding asphaltene and oil fractions). These trends appear to suggest that the iron catalyst in the presence of carbon monoxide gives a better quality product than without carbon monoxide -- and under these conditions, on the order of the molybdenum catalyzed conversion. However, although we are using the same type of autoclave for these different catalysts, we are conducting the iron catalyzed reactions in a different autoclave than with the molybdenum catalyzed conversions,. In past work we have found that for reactions with a high solids content, as with these reactions, there may be slightly different conversion yields between the two reactors, most likely due to slightly different stirring rates or depth of stirrer, so we do not want to make a direct comparison of the two catalyst types at this time.

Table 1

ANALYSES OF CONVERSION PRODUCTS[a]

Conversion	Atmosphere	%C	%H	H/C	O
Black Thunder		63.56	4.96	0.930	
Recycle Vehicle[b]		88.08	7.09	1.055	
Fractionated Recycle Vehicle					
THF-Insol		42.55	2.59	0.726	
Preasphaltene		85.61	5.76	0.801	
Asphaltene		87.21	9.58	1.309	
Oils		89.37	10.54	1.404	
Recycle Conversion Products	1000 psi H_2				
THF-Insol		30.62	1.62	0.632	
Preasphaltene		86.32	4.62	0.637	
Aspahltene		87.84	6.21	0.842	
Oils		84.20	8.10	1.145	
Recycle/$Fe(CO)_5$	1000 psi				
THF-Insol	50% CO	78.27	-	-	
Preasphaltene	1 mL H_2O	83.25	3.98	0.570	
Asphaltene		88.96	7.87	1.054	
Oils		87.31	11.19	1.526	
$Fe(CO)_5$	1000 psi H_2				
THF-Insol		36.92	1.82	0.587	
Preasphaltene		86.86	4.94	0.676	
Asphaltene		86.71	6.49	0.891	4.78
Oils		88.66	8.93	1.199	2.37
$Fe(CO)_5$	1000 psi				
THF-Insol	20% CO	36.31	-	-	
Preasphaltene	-	-	-	-	
Asphaltene		89.05	7.10	0.949	
Oils		88.39	12.11	1.632	
$Fe(CO)_5$	1000 psi				
THF-Insol	20% CO	47.48	2.37	0.594	
Preasphaltene	1 mL H_2O	90.43	4.85	0.639	
Asphaltene		88.58	7.16	0.962	
Oils		84.61	7.90	1.112	
$Fe(CO)_5$	1000 psi				
THF-Insol	50% CO	47.17	-		
Preasphaltene		85.02	-		
Asphaltene		89.14	7.14	0.954	2.74
Oils		84.06	11.06	1.566	1.74
$Fe(CO)_5$	1000 psi				
THF-Insol	50% CO	46.49	-	-	
Preasphaltene	0.5 mL H_2O	83.94	-	-	
Asphaltene		88.13	7.18	0.969	
Oils		87.73	11.19	1.519	
$Fe(CO)_5$	1000 psi				
THF-Insol	50% CO	45.81	-	-	
Preasphaltene	1 mL H_2O	80.18	4.85	0.720	
Asphaltene		88.03	7.95	1.076	2.68
Oils		88.93	10.04	1.345	1.76
MolyVanL	1000 psi H_2				
THF-Insol		54.41	-	-	
Preasphaltene		79.95	-	-	
Asphaltene		88.98	7.17	0.960	2.90
Oils		87.14	10.74	1.468	1.83

[a] Reaction conducted in a 300-mL autoclave with 20 g Black Thunder Wyodak coal, 1.4 g iron metal in catalyst, 50 g recycle solvent and at 425°C. Atmosphere contained 3% H_2S in either H_2 or CO/H_2.

[b] Approximately 37% distilate, 18% Cl, and 45% resid.

TASK 2: LABORATORY SCALE OPERATIONS

The objectives of the first phase of this task are to evaluate the effects of dispersed catalysts and carbon monoxide containing atmospheres in the first stage of a 2-stage liquefaction process. We are continuing our work to evaluate the base-line first-stage reaction conditions, with experiments being run at 425°C for 1 hour in a 300 mL autoclave. The feedstock consisted of 2.5 parts by weight of recycle solvent from Wilsonville run #263 (50g) to 1 part Black Thunder coal (20g). The total gas content is 1000 psi (cold charge). The coal was dried at 76°C under <1 torr vacuum to reduce the water content, since the Wilsonville coal facility dries their coal prior to conversion. In addition to the Black Thunder conversions, we also conducted several experiments designed to test the effects of the catalyst on coal conversions in the presence of an inert solvent. We were prompted to conduct these experiments because H-donor solvents and especially recycle vehicles, tend to moderate the effects of the catalyst making it difficult to study differences in reactivities and selectivities.

Black Thunder Conversions

The purpose of this quarters experiments using the Black Thunder coal were to compare the effects of added water, and the comparative effect of molybdenum versus iron. As described last quarter, when a small amount of water (1 mL) was added to the runs of iron carbonyl with carbon monoxide atmospheres in an attempt to increase the extent of the water-gas-shift reaction, a decrease in oils was observed. This quarter, in order to determine if this unexpected behavior involved the coal itself, we conducted a similar conversion in the presence of the recycle vehicle with catalyst and carbon monoxide atmosphere, but without the coal, and again found a decrease in oils. The conversions and product profiles of the Black Thunder conversions are listed in Table 2, and are determined on a MAF basis. Conversions to THF soluble materials were calculated according to equation 1, which was derived in Quarterly Report 8.

$$100 - [(\text{Wt fraction} - 4.9)/28.6^{*}]\text{x}100 \qquad (1)$$

* = % Coal in feed

As seen in Table 2, conversions of the recycle vehicle under a hydrogen atmosphere and no water or catalyst, yielded 30.9% oils, whereas with catalyst and water, and in carbon monoxide atmospheres, yielded only 18.7% oils. Although the conditions are very much different, it would seem unlikely that the addition of catalyst to the recycle vehicle would decrease the oil formation. The addition of carbon monoxide will decrease the partial pressure of hydrogen, and may therefore allow more dehydrogenation reactions, causing more coking. However, this effect would be expected more with the asphaltenes than with the oils. In previous experiments the carbon monoxide has shown improvements in oil production during the coal conversions. For instance, with 50% atmosphere an oil yield of 26% was achieved compared to only 22% under a hydrogen atmosphere. The addition of water, however, reduced the oil yield to only 7% when 1 mL of water was added, but had only a negligible effect when 0.5 mL was added. FIMS analysis of the these products shows that the major effect between these fractions is that the toluene soluble fractions from the 1 mL water treatment had an enhanced amount of lower molecular weight materials. Thus the effect of water still is not clear but it appears that some of the material normally extracted into the hexane fraction remains in the toluene fractions; perhaps the effect of water is to increase the polarity of the fractions. Nevertheless, water does not increase the yields of oils, and since water is difficult to deal with during coal conversions anyway, we see no need in pursuing the question at this time.

We also conducted molybdenum catalyzed conversions using MolyVanL. We found that the reaction produced a considerable amount of hydrogen consumption and gave a better quality product in terms of lower viscosity than the iron catalysts, as expected. However, the overall yields in terms of coal conversion to THF soluble products was not any better than the iron catalysts. We suspect that this anomaly is primarily due to the very poor quality of the recycle vehicle, which instead of acting as a hydrogen donor, is merely being further hydrogenated and little coal conversion is occurring. Further differences in conversions may be due to using a different 300 mL autoclave which may have slightly different properties such as stirring rate or depth of stirrer. We have attributed such slight differences to differences in coal conversions with high solids content as in these reactions. However, we would expect that this catalyst will perform better under higher hydrogen pressures.

Model Coal Conversions

To further expand on the differences between various catalysts, conversions were also conducted in a non-reactive solvent, n-hexadecane. The advantage of conversions in this solvent is

Table 2

MAF YIELDS OF FRACTIONATED PRODUCTS[a]

Catalyst	Atmosphere	THF Insol	Preasphaltene	Asphaltene	Oils	
Recycle	as received	8.7	7.5	60.9	23.2	-
Recycle	1000 psi H_2	6.9	4.6	53.2	30.9	-
Recycle $Fe(CO)_5/H_2O^c$	1000 psi CO/H_2	15.7	4.3	58.4	18.7	-
$Fe(CO)_5$	1000 psi H_2	5.8	7.5	54.9	21.7	96.9
$Fe(CO)_5$	20% CO/H_2	9.9	5.0	40.1	21.5	82.5
$Fe(CO)_5/H_2O^c$	20% CO/H_2	14.2	11.9	54.9	4.6	67.5
$Fe(CO)_5$	50% CO/H_2	15.4	19.2	35.8	26.1	63.3
$Fe(CO)_5/H_2O^c$	50% CO/H_2	14.3	14.4	47.6	7.4	67.1
$Fe(CO)_5/H_2O^d$	50% CO/H_2	15.1	9.4	34.8	25.0	64.3
MolyVanL[e]	1000 psi H_2	21.2	9.1	33.2	20.7	43.0

[a] Reaction conducted in a 300-mL autoclave with 20g Black Thunder Wyodak coal, 1.4 g iron metal in catalyst, 50 g Recycle solvent and at 425°C. Atmosphere contained 3% H_2S in either H_2 or CO/H_2.
[b] Coal Conversion = 100 - [(THF Insol -4.9)/28.6]x100
[c] 1 mL H_2O added.
[d] 0.5 mL H_20 added.
[e] 500 ppm Mo added.

we can distinguish between the effects of the solvent and the catalyst, since the recycle vehicle as used above, and H-donor solvents such as tetralin tend to overwhelm the effect of the catalyst.

These model coal liquefaction experiments were conducted in a 300 mL Autoclave Engineers stirred reactor using 5.0 g of coal, 3 mmol of catalyst, 30 g of solvent, and 500 psig (cold) hydrogen. Reaction temperatures were held at either 400°C or 425°C for 20 minutes. The product was filtered through a medium porosity filter and separated into toluene soluble (TS) and insoluble (TI) fractions. The coals used were PSOC 1098 Illinois #6, and Beulah-Zap seam North Dakota lignite from the Argonne Premium coal bank.[11] Conversions were calculated from the amount of toluene-insoluble material and are on a maf basis for the Illinois #6 coal and on a carbon basis for the Lignite.

The organometallic molybdenum catalyst was $(C_5H_5)_2Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$, referred to as Mo(OM), and was prepared by modification of the method of Dubois et al.[12] Pentacarbonyl iron was obtained from Aldrich, and the sulfur-containing iron cluster, $(\mu\text{-}S_2)Fe_2(CO)_6$, referred to as Fe_2S_2, was prepared by the method of Bogan et al.[13] Ammonium tetrathiomolybdate, (MoS_4), was obtained from Alfa Chemicals. Nickel biscyclooctadiene [$Ni(COD)_2$] was obtained from Organometallics Inc.

Data from coal conversions in tetralin and hexadecane solvent systems are presented in Table 3. The first four liquefaction experiments listed were conducted at 400°C and include a non-catalyzed conversion, and conversions using molybdenum (MoS_4 and Mo(OM)) catalysts on an Illinois #6 coal. The remaining four experiments were conducted at 425°C for an Argonne Lignite coal, and compare various soluble iron and nickel based catalysts. Since conversions in tetralin appeared to moderate the effects of the catalysts, we were prompted to utilize a non-reacting, non-donor conversion medium that would not interfere with the study of the catalysts. In order to achieve this goal, conversions were conducted in n-hexadecane so that solvent interactions should be minimal. In previous work we have observed no decomposition of n-hexadecane under these conditions. Most of the conversions are quite low, as expected. For instance in the absence of catalyst the Illinois #6 coal was converted to 25% toluene soluble material. However, in the presence of the molybdenum catalysts, the conversions were greatly enhanced. The coal impregnated with MoS_4 of 41% and the organometallic molybdenum-impregnation [Mo(OM)] resulted in a conversion of 54%, which is nearly as great as when tetralin was used as the conversion medium. Thus we suggest that if the catalyst dispersion is great enough, and does not require high temperature activations, good liquefaction solvents are not necessary.

The last four conversions are of an Argonne Lignite. As shown in the table both the soluble organometallic iron complexes ($Fe(CO)_5$ and ($FeS_2(CO)_2$)) are very effective for low rank coals, giving conversions in the range of 40%; however, when the nickel catalyst was used, the conversions increased to 60%. Iron catalysts are well known to be effective for liquefaction of low rank coals. However, nickel has been rarely used. Since low rank coals are high in carboxylates, and nickel is known to aid in decarboxylations, it would seem that dispersed catalysts containing nickel should also be examined for low rank coals.

Table 3

CONVERSION TO TOLUENE SOLUBLE PRODUCTS IN HEXADECANE[a]

Catalyst	Coal	T(°C)	% TS[b]
None	Illinois # 6	400	25
Mo(Aq)	Illinois #6	400	41
Mo(OM)	Illinois #6	400	54
Mo(OM)[c]	Illinois #6	400	61
None	Lignite	425	24
$Fe(CO)_5$	Lignite	425	41
Fe_2S_2	Lignite	425	39
$Ni(COD)_2$	Lignite	425	60

[a] Reaction conducted in a 300-mL autoclave with 5 g coal, 3 mmol catalyst, 30 g solvent and 500 psi H_2 for 20 min at temperature.

[b] Yields calculated on maf basis for Illinois #6 coal and on a carbon basis for lignite.

[c] Reaction run in tetralin under identical conditions.

REFERENCES

1. S. N. Rao, H. D. Schindler, and G. V. McGurl, ACS Fuel Preprints,(1988) **33**(3), 145-156.
2. J. M. Lee, O. L. Davies, T. E. Pinkston, and J. R. Gough, ACS Fuel Reprints, (1988) **33**(3), 157-171.
3. D. Gray and G. Tomlinson, ACS Fuel Preprints (1988) **33**(3), 172-179.
4. S. V. Gollakota, J. M. Lee, O. L. Davies, and T. E. Pinkston, DOE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, Pennsylvania, October 1988.
5. R. Neavel, Phil. Trans. R. Soc. Lond. A, (1981) **300,** 141.
6. E. C. Moroni, ACS Fuel Preprints, (1986) **31**(4), 294-299.
7. E. M. Suuberg, D. Lee, and J. W. Larsen, Fuel, (1985) **64**, 1668.
8. G. V. Deshpande, P. Solomon and M. A. Serio, ACS Fuel Preprints, (1988) **33**(2), 310.
9. E. C. Moroni, ACS Fuel Preprints, (1988) **33**(1), 384-386.
10. C.-L. Li, Z.-r Xu, and B. Gates, Ind. Eng. Chem. Prod. Res. Dev., (1985) **24**, 92-97.
11. Vorres, K., Energy and Fuels (1990) **4**, 420-426.
12. Cowens, B. A., Haltiwanger, R. C., and DuBois, M. R., Organometallics (1987) **6**, 995-1004.
13. Bogan, L. E. Jr., Lesch, D. A., and Rauchfuss, T. B., J. Organometallic Chem. (1983) **250**, 429-438.

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