UPGRADING COAL LIQUEFACTION RECYCLE BOTTOMS

H. F. Silver, R. L. Miller and R. G. Corry
Chemical Engineering Department

R. J. Hurtubise
Chemistry Department

University of Wyoming, Laramie, Wyoming 82071

INTRODUCTION

In both the EDS and the SRC-II direct coal liquefaction processes, distillate yields have been increased significantly by including vacuum column bottoms product in the recycle solvent. While the distillable portion of the recycle solvent is upgraded in the EDS process, no specific effort is made to upgrade the non-distillable portion of the recycle solvent in either the EDS nor the SRC II processes. A study was therefore initiated at the University of Wyoming to determine the effect of upgrading coal liquefaction recycle bottoms.

EXPERIMENTAL PROCEDURE

Liquefaction of both subbituminous Wyodak and bituminous Kentucky coals has been studied in a two-liter Autoclave Magnedrive-II batch reactor. Samples of Wyodak coal, Wyodak coal derived recycle solvent, and solvent refined coal, SRC, were supplied by Catalytic, Inc. from the Southern Services Inc. pilot plant at Wilsonville, Alabama. Samples of Kentucky coal, Kentucky coal derived recycle solvent and SRC were supplied by the Pittsburg & Midway Coal Mining Co. from their pilot plant near Tacoma, Washington.

Portions of the recycle solvents boiling above 533K were used as received while other portions were mildly hydrogenated over a Co-Mo on Al_2O_3 catalyst (Nalcomo 477) for 60 minutes at 644K using an initial cold reactor hydrogen pressure of 13.8 MPa. Portions of the SRC were used as received while other portions were upgraded by solvent fractionation and by hydrogenation. The SRCs were solvent fractionated into cyclohexane soluble oils, cyclohexane insoluble - benzene soluble asphaltenes, benzene soluble oils plus asphaltenes and benzene insoluble-pyridine soluble preasphaltenes. Portions of the SRCs and their oil plus asphaltene fractions were mildly hydrogenated over catalyst at 644K for 60 minutes using an initial cold reactor hydrogen pressure of 13.8 MPa. Other portions were severely hydrogenated over catalyst at 700K for 60 minutes using an initial cold reactor hydrogen pressure of 20.7 MPa.

Coal liquefaction experiments were then conducted by charging the reactor with recycle solvent, SRC or SRC fraction and coal in a 1:1:1 weight ratio. The reaction was carried out at 714K for 60 minutes using an initial cold reactor hydrogen pressure of 13.8 MPa. Gaseous products were analyzed using an HP 5840 gas chromatograph. Liquid products were distilled using a modified ASTM-D 1160 apparatus. Unreacted coal and mineral matter were determined by soxhlet extractions using pyridine. All runs were duplicated.

DISCUSSION OF RESULTS

The extent of coal liquefaction in this work was measured using percent 700K+ conversion, X_{700}, defined by the relationship

$$X_{700} = \frac{W_{IN} - W_{OUT}}{W_{IN}} \times 100$$

where W_{IN} = grams of MAF coal plus grams of SRC or SRC fraction plus grams of 700K+ distillate charged to the reactor.

and W_{OUT} = grams of MAF 700K+ product recovered from the reactor.

A summary of the conversions obtained using different solvents is presented in Table I. The average reproducibility of conversions for duplicated runs was within ± 1.0% of the mean values reported in this table.

Examination of the results for solvents 1-6, containing Wyodak coal derived SRC, and solvents 12-16, containing Kentucky coal derived SRC, suggest that maximum conversions are obtained if the SRC is mildly hydrogenated. The data obtained from Wyodak solvents 4, 5 and 6, and for Kentucky solvents 13, 14 and 16 suggest that SRC component effectiveness may pass through a maximum as hydrogenation severity is increased. Comparison of solvent 3 with solvent 5 and solvent 15 with solvent 16 suggests that the observed increases in conversion relative to solvents 1 and 12 are due more to mildly hydrogenated SRC than mildly hydrogenated distillate.

While the relatively high conversion obtained from solvent 2 could be attributed to the catalytic activity of the ash in this sample of unfiltered SRC, ash found in Wyodak coal is generally not considered to be a catalyst for the coal liquefaction reaction. A more reasonable explanation for the high conversion observed when using solvent 2 is the lower initial boiling point of the high ash SRC as compared to the filtered SRCs. In the pilot plant, ash increases the viscosity of SRC. In order to reduce this viscosity, some of the normally distillable liquids were not removed from the high ash SRC during distillation.

The results shown in Table I also suggest that solvent fractionation may also improve the liquefaction effectiveness of SRCs. Results obtained using solvents 17-19 suggest that little, if any, improvement in Kentucky coal solvent effectiveness can be obtained by hydrogenating the benzene soluble oils plus asphaltenes obtained from Kentucky SRC.

Liquid yields and hydrogen consumption depend upon the extent of coal conversion. Net liquid yields of C_4-533K and 533-700K from Wyodak coal as a percent of the MF coal are presented in Figures 1 and 2 as a function of X_{700}. Points presented on these and the following figures are identified by the number in Table I identifying the solvent used in the experiment. As would be expected, liquid yields increase with increasing X_{700}. Similar plots of liquid yields for Kentucky coal are presented in Figures 3 and 4. For comparison purposes, the solid lines in Figures 1 and 2 have been reproduced as dashed lines in Figures 3 and 4, respectively, so that direct comparisons can be made between Wyodak and Kentucky coal yields. As can be seen in Figures 3 and 4, Kentucky coal produced greater liquid yields than Wyodak coal at low conversions. However, at high conversions, the liquid yields from the two coals are quite comparable.

Hydrogen consumptions for both Wyodak and Kentucky coal experiments are presented in Figures 5 and 6. The consumptions shown in these figures do not include the hydrogen consumed in upgrading either the distillable solvent nor the SRC or SRC fractions. It has been estimated that hydrogen consumed in this manner would be in the order of 1.0 to 2.0 wt% of the MAF coal charged to the reactor.

CONCLUSIONS

Results obtained from this work indicate the importance of solvent composition on the coal liquefaction reaction. Through the addition of mildly hydrygenated SRC to a recycle solvent, for example, net C_4-700K liquid yields approaching 60 wt% of the MF coal charged to a batch reactor were obtained from both Wyodak and Kentucky coals used in this study.

A certain amount of bottoms recycle upgrading may occur indirectly in processes such as the EDS process with bottoms recycle or the SRC-II process. However, it may be possible to obtain even further increases in distillate yields by direct upgrading of a bottoms recycle, either by hydrogenation or by solvent fractionation. It should be pointed out that these hypotheses are based on batch reactor runs, simulating continuous coal liquefaction operation. Deleterious compounds could build up in recycle streams in continuous plants that were not observed in this study. Further work in this area appears to be warranted.

ACKNOWLEDGEMENTS

Mr. Ronald Borgialli and Mrs. Jane Thomas have made substantial contributions to this program. The work has been carried out under DOE Contract No. DE-AC01-79ET14874.

TABLE I

X_{700} CONVERSION RELATED TO THE DEGREE OF SOLVENT HYDROGENATION

COAL	SOLVENT NO.	SOLVENT: DISTILLABLE PORTION	SOLVENT: NONDISTILLABLE PORTION	X_{700} (%)
WYODAK	1	UH(1)	SRC, UH	23.8
	2	UH	(SRC+Ash), UH	36.5
	3	UH	SRC, MH(2)	42.5
	4	MH	SRC, MH	35.8
	5	MH	SRC, UH	32.0
	6	MH	SRC, SH(3)	27.2
	7	UH	(O+A)(4), UH	28.4
	8	MH	(O+A), MH	37.4
	9	MH	(O+A), SH	29.0
	10	UH	A(5), UH	34.6
	11	UH	O(6), UH	35.9
KENTUCKY	12	UH	SRC, UH	28.5
	13	MH	SRC, MH	39.9
	14	MH	SRC, SH	36.4
	15	UH	SRC, MH	38.8
	16	MH	SRC, UH	30.5
	17	UH	(O+A), UH	35.5
	18	MH	(O+A), MH	37.0
	19	MH	(O+A), SH	37.0

NOTES:
(1) UH = Unhydrogenated
(2) MH = Mildly Hydrogenated
(3) SH = Severely Hydrogenated
(4) O+A= Oils plus Asphaltenes
(5) A = Asphaltenes
(6) O = Oils

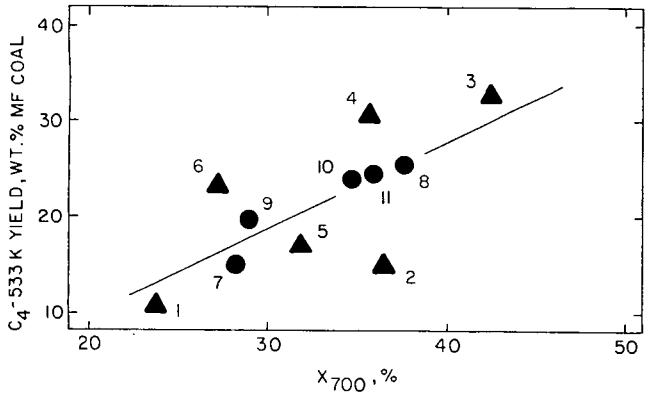

Figure 1. C_4-533K Wyodak Coal Liquid Yields as a Function of X_{700}

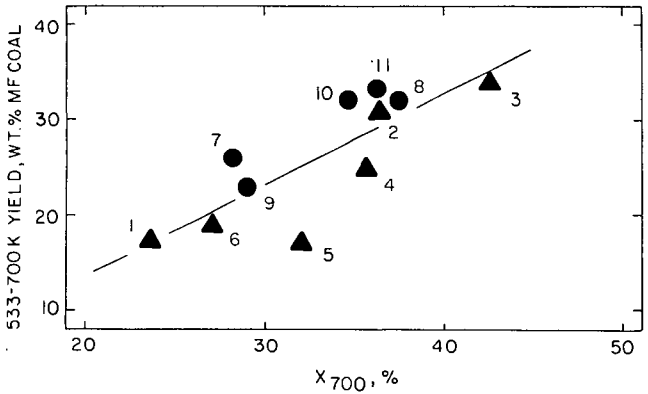

Figure 2. 533-700K Wyodak Coal Liquid Yields as a Function of X_{700}

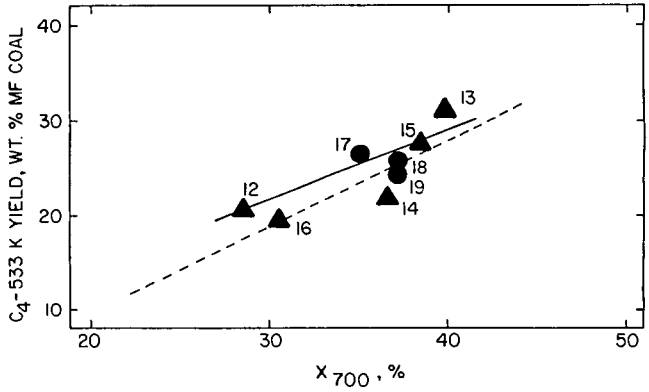

Figure 3. C_4-533K Kentucky Coal Liquid Yields as a Function of X_{700}

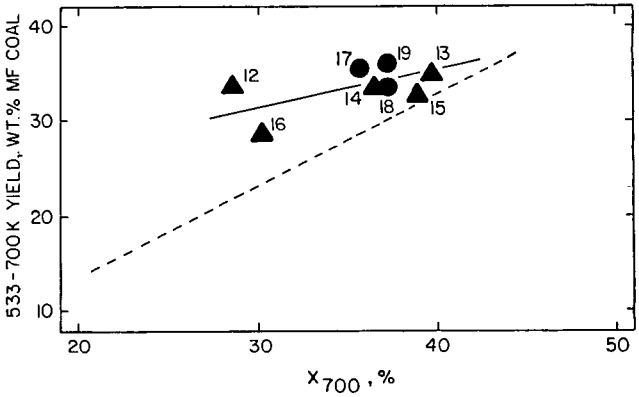

Figure 4. 533-700K Kentucky Coal Liquid Yields as a Function of X_{700}

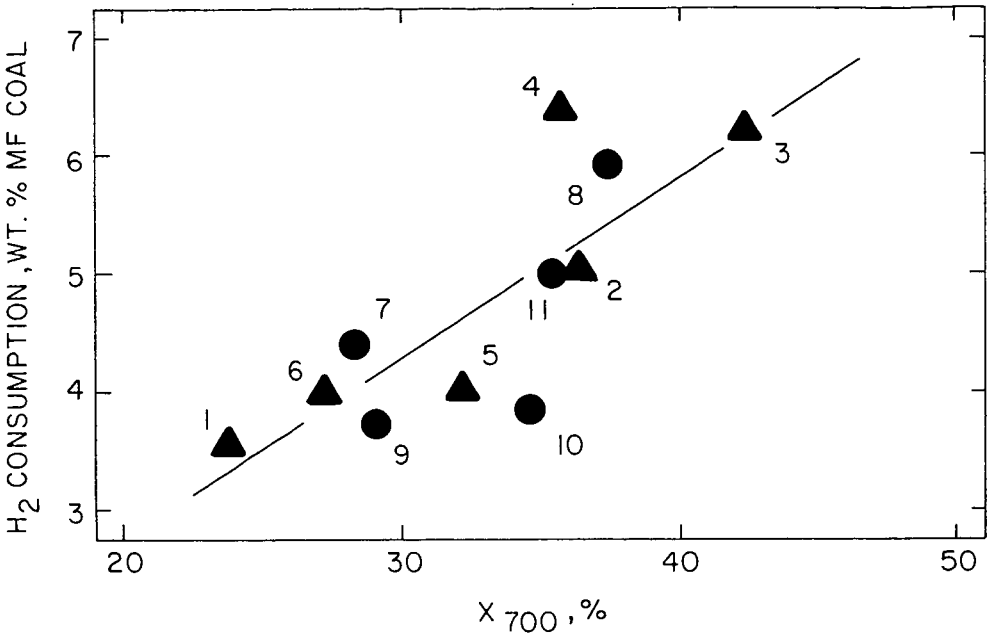

Figure 5. Hydrogen Consumption for Wyodak Coal as a Function of X_{700}

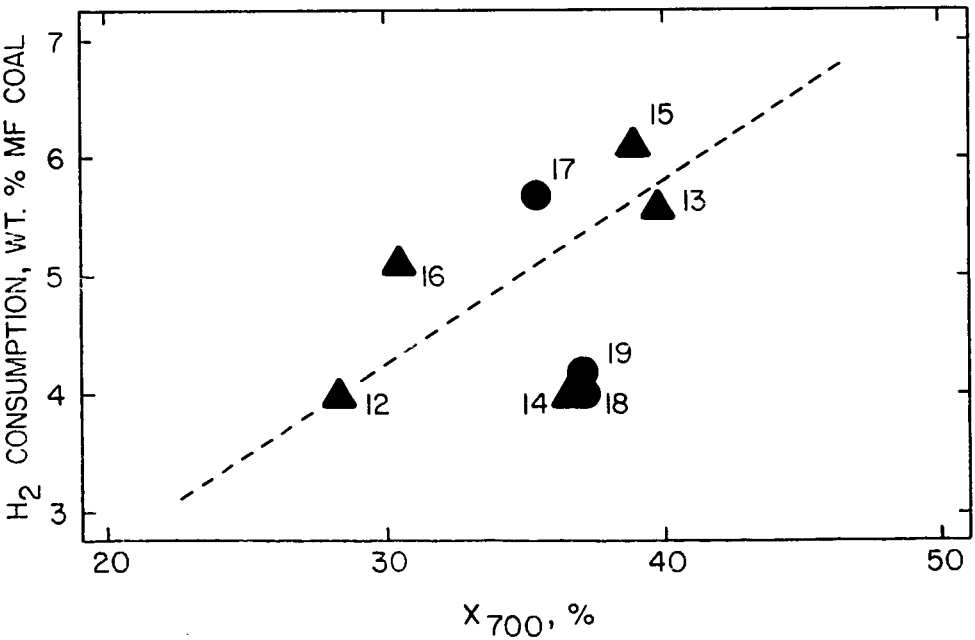

Figure 6. Hydrogen Consumption for Kentucky Coal as a Function of X_{700}