

HIGH LIQUID YIELDS FROM BITUMINOUS COAL VIA
HYDROPYROLYSIS WITH DISPERSED CATALYSTS

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INTRODUCTION

In some respects, coal hydroxyprolysis is potentially a more attractive route for the production of liquid fuels than direct liquefaction techniques utilizing solvents. It offers a process configuration that avoids the use of a recycle solvent, which constitutes up to two-thirds of the reactor feed stream. However, historically, pyrolysis processes have been associated with low conversions of coal to liquid products (1-3), making char the principal product for which some application, apart from providing process heat and hydrogen, must be found. Moreover, large quantities of methane are usually produced during hydroxyprolysis at temperatures above 600°C which are required to achieve substantial liquid yields. Consequently, hydrogen consumptions are high. Results of two-stage hydroxyprolysis studies, in which primary tar vapors are passed through a catalyst bed, previously reported by several of the authors (4-6) have shown that daf yields of 20-25% distillate along with only 3-4% methane can be achieved if non-catalytic hydroxyprolysis of bituminous coal, carried out at a pressure of about 150 atmospheres and a temperature of 500°C, is followed by catalytic upgrading of the tar at a temperature of 400°C.

Early work (7,8) established that coals could be catalytically hydrogenated in batch reactors in the absence of a solvent to give high conversions to pyridine soluble materials. Impregnated molybdenum catalysts were among the most active studied. More recent work (9) has demonstrated that dispersed sulfided Mo is effective under mild conditions; over 50% chloroform soluble material can be generated from bituminous and subbituminous coals by reaction at 400°C and a cold-charge hydrogen pressure of 70 atmospheres. Lewis acids, such as zinc and stannous chlorides, have been shown to enhance liquid yields (10,11), but relatively large concentrations of catalyst are required. Early work has shown that Mo could be used to achieve hydroxyprolysis yields exceeding the proximate volatiles content (12,13). However, sulfided Mo, which is thought to be the most active form for coal conversion, was not used. Moreover due to the high temperatures and pressures used, secondary reactions could not be controlled giving rise to a low selectivity to liquid products.

In this paper we report the results of catalytic hydroxyprolysis experiments in which greater than 60% daf coal basis yields of tar are produced with weight ratios of tar to gases up to 80% higher than observed in an uncatalyzed reaction. The work has also shown that dispersed sulfided molybdenum and hydrous titanium oxide (HTO) catalysts coated directly on the coal are superior to Lewis acids and alumina supported hydrogenation catalysts in terms of tar yields achieved and reduction of the amount of light hydrocarbon gases produced. In addition, we have performed two-stage hydroxyprolysis tests which demonstrate that the tar produced is readily upgraded.

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EXPERIMENTAL

Coal and Catalysts

A high volatile UK bituminous coal (Linby), ground to 75 to 150 micron particle size range, was used for these tests. Analysis of the coal has been reported elsewhere (4). Catalysts used for these tests were 1) zinc and stannous chloride Lewis acids, 2) a commercial Ni-Mo/alumina, 3) bulk HTO (14,15) formulations (Pd and Co-Ni-Mo), 4) coatings of Ni and Pd HTOs and 5) dispersed sulfided Mo. Lewis acid catalysts were impregnated into the coal from aqueous solution. Powdered (-200 mesh) alumina supported and bulk HTO catalysts were physically mixed with the coal, the catalyst weight being 20% daf coal. Ni and Pd HTO catalyst coatings were dispersed by coating the coal with sodium hydrous titanium oxide (Na HTO) followed by contact of the Na HTO-coated coal with aqueous solutions of either Ni or Pd. This resulted in the active metal being incorporated into the hydrous titanate coating via ion exchange for Na⁺. Finely divided MoS₂ was dispersed by wetting the coal with solutions of (NH₄)₂MoS₄ or (NH₄)₂MoO₂S₂. The amounts of active metals in all the materials are given in Table I.

Apparatus and Procedure

The hydropyrolysis reactor and procedures used for the tests have been described previously (4,5). Most of the tests were single-stage catalytic hydropyrolysis experiments, carried out at 150 atmospheres hydrogen pressure and 500°C. The hydropyrolysis zone was heated at a rate of 5°C/s from ambient and held at temperature for 10 min. Hydrogen was passed downward through the reactor at a flow rate equivalent to 5 l/min at standard temperature and pressure and tars were collected in an ice-cooled trap. For comparison with the catalytic experiments, a single-stage test was also performed without catalyst. In addition, two two-stage experiments were performed: the first with a non-catalytic hydropyrolysis stage followed by a presulfided Ni-Mo/alumina catalytic upgrading stage (5,6) operated at 400°C, and the second with dispersed MoS₂ catalyst (0.6% Mo, daf coal basis) in the hydropyrolysis stage followed again by presulfided Ni-Mo/alumina catalyst in the second stage.

Product Recovery and Analysis

Gas exiting the reactor was collected and analyzed for C₁-C₄ hydrocarbons, CO and CO₂. Following the completion of each experiment, the post-reaction contents of the reactor tube were removed and weighed to determine the char and ash remaining. Liquid products contained in the reactor product cold trap were first weighed, then recovered with dichloromethane (DCM). Water was removed using phase separating paper and weighed, and the DCM solutions were evaporated to give tar samples for analysis. The daf coal basis percentage yield of tar for each experiment was calculated as the weight of material recovered in the cold trap less the weight of water produced. The tars were subjected to a variety of analyses to determine the elemental composition--including oxygen concentration, phenolic OH, aromatic hydrogen content, and number average molecular weight. For the two-stage experiments, the liquid products exiting the second stage of the reactor were recovered neat in order to determine the fraction of light naphtha.

RESULTS AND DISCUSSION

Single-Stage Hydropyrolysis

The products resulting from the single-stage catalytic hydropyrolysis experiments, classified as tar, methane, C₂-C₄ hydrocarbons, and char, are listed in Table I. For comparison with the catalytic experiments, the distributions for a non-catalytic experiment are included. As can be seen in Table I, all of the catalyzed

experiments produced significantly more tar than the non-catalytic case. Examination of the results for the various catalysts indicates that tar yields and product selectivity are dependent on the catalyst or active metal employed and the technique used to disperse the catalyst with the coal. The greatest tar yields, 59-64%, were achieved with well-dispersed catalysts containing metals known to be active for coal conversion.

The effect of the active metal may be seen by comparison of the experiments with Ni and Pd HTO coatings and MoS₂. As anticipated, the Pd and Mo catalysts gave higher tar yields (~60%) than the Ni catalysts (~50%). With respect to dispersion, Pd HTO catalysts coated onto the coal and the MoS₂ dispersed from aqueous solution gave higher yields than the Pd HTO and Ni-Mo/alumina finely divided catalyst powders which were physically mixed with the coal, even though the coal basis amount of active metal was significantly greater for the powdered catalysts. The Lewis acid catalysts, ZnCl₂ and SnCl₂, dispersed onto the coal from aqueous solution, produced tar yields of 36% and 54%, respectively, despite the five-fold difference in catalyst weight. This result suggests that further experiments are also needed with Ni and Pd HTO catalyst coatings to determine the minimum amount of active metal required to achieve high yields. Indeed, we have performed experiments similar to those reported here that showing that concentrations of Mo as low as 0.1% can be used without sacrificing tar yield.

In general, C₁-C₄ hydrocarbon gas formation increased with the increase in tar yield. For most of the catalytic experiments, the amount of methane formed (2-4%) was nearly equal to that for the non-catalytic experiment (3%). However, the Lewis acid catalysts produced significantly more methane (6%). The yield of C₂-C₄ hydrocarbon gases produced by the non-catalyzed case was 4%; the catalyzed experiments produced yields from 4 to 9%. Because liquids are the desired hydropyrolysis products, and gaseous hydrocarbons are not only of low value but result in wasteful consumption of hydrogen, a useful figure of merit, shown in Table I, for comparison of the efficiency of conversion is the selectivity defined in terms of the weight ratio of tar to gas yield. Compared to the selectivity for the non-catalyzed experiment, 3.7, the selectivities for the Lewis acid catalysts, 2.8 and 4.1, at best offer little improvement. However, the other catalysts show relative improvement in selectivity ranging from 35 to 80%.

Two-Stage Hydropyrolysis

The two-stage experiments were performed to demonstrate that the tar produced in greater yields from catalyzed hydropyrolysis can be hydrotreated in a second stage to produce a high quality liquid product. Table II shows the compositions of the primary tars produced by non-catalytic and catalytic hydropyrolysis, along with the compositions of the products resulting from second-stage vapor-phase hydrotreatment of the primary tars with presulfided Ni-Mo/alumina catalyst. First-stage product distributions in terms of yields of tar, hydrocarbon gases, and char are given in Table I for similar non-catalyzed and MoS₂ catalyzed experiments. As can be seen from the two tables, tar yield for the catalyzed product was double that for the uncatalyzed product in the single-stage experiments, and although the H/C ratio, aromatic hydrogen and nitrogen contents for both primary tars were similar after the first stage of the two-stage experiments, the oxygen and sulfur contents of the catalyzed hydropyrolysis tar were significantly less than those for the uncatalyzed tar. In addition, the number average molecular weight of the tar produced by the catalyzed experiment was only slightly greater than that produced by uncatalyzed hydropyrolysis.

The composition and average molecular weights of the tars described above indicate that upon hydrotreatment they should yield liquids of similar composition.

Examination of the analyses for the hydrotreated products of the tars shows this to be an accurate assumption. However, two significant differences were noted: the product resulting from the catalytically produced hydroprolysis tar had a lower H/C ratio, but a greater daf coal basis yield of light naphtha.

CONCLUSION

Although hydroprolysis processes have been historically associated with high yields of methane and light hydrocarbon gases, and low yields of total liquid products, the experiments described in this paper demonstrate otherwise. We have shown that with the proper choice of catalysts and reaction conditions, two-stage catalytic hydroprolysis can achieve yields of high-quality liquids rivaling those for two-stage direct liquefaction processes which utilize a recycle solvent. In addition, the yield of low value hydrocarbon gases can be minimized. Use of catalytic hydroprolysis to convert coal to liquid fuels may offer advantages associated with elimination of the recycle solvent, which constitutes two-thirds of the mass of the reactor feed in traditional direct liquefaction processes. However, in order to be economically feasible, processing technology must be developed to use low catalyst concentrations or to permit addition, withdrawal, regeneration and recycle of the first-stage hydroprolysis catalyst. This, of course, is a task requiring a great deal of additional effort.

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TABLE I. Product Distributions Resulting from Single-Stage Hydropyrolysis Experiments¹

CATALYST (daf Coal Basis Wt % Active Metal)	TAR	METHANE	C ₂ -C ₄ HYDROCARBONS	CHAR	SELECTIVITY Prod. Wt. Ratio (tar/gas)
None	26	3	4	60	3.7
ZnCl ₂ (5%)	36	6	7	45	2.8
SnCl ₂ (1%)	54	6	7	30	4.1
Ni-Mo/Alumina (3.6%)	42	3	4	42	6.0
CoNiMo HTO-bulk (2.9%)	38	2	4	46	6.3
Pd HTO-bulk (2.0%)	47	3	4	35	6.7
Ni HTO coating (0.5%)	50	4	6	32	5.0
Ni HTO coating (1.0%)	53	4	6	29	5.3
Pd HTO coating (0.7%)	64	3	9	16	5.3
Pd HTO Coating (1.6%)	62	4	7	20	6.2
MoS ₂ (0.6%)	59	4	6	20	5.9

1. Products are given on a Wt.% daf coal basis and included -6% water and -2% CO + CO₂.

TABLE II. Composition of Primary Hydropyrolysis Tar and Second-Stage Product for Experiments With and Without a Catalyzed First Stage¹

<u>Primary Tar Composition</u>	<u>Uncatalyzed First Stage</u>	<u>Catalyzed First Stage²</u>
C	84.3	86.1
H	6.8	7.0
O Wt % of product	5.3	3.6
N	1.5	1.7
S	0.9	0.4
OH	4.3	3.0
H/C atomic ratio	0.97	0.98
% Aromatic H of total H	36	33.5
M _n -number ave. mol. wt.	250	270

Second-stage Product³

C	84.0	88.0
H Wt % of product	13.6	11.9
OH	0.01	0.05
ppm N	7	33
H/C atomic ratio	1.94	1.62
% Aromatic H of total H	4	7
Light Naphtha (Wt % daf coal)	8.3	11.2

1. First Stage Conditions - 500°C, 150 atm hydrogen pressure.
 Second Stage Conditions - 400°C, 150 atm hydrogen pressure.
2. First Stage Catalyst - 0.4%, coal basis, MoS₂.
3. Second Stage Catalyst - Ni-Mo/alumina.