Examination of Alternative Catalysts for Biomass Direct Liquefaction

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FOR BIOMASS DIRECT LIQUEFACTION

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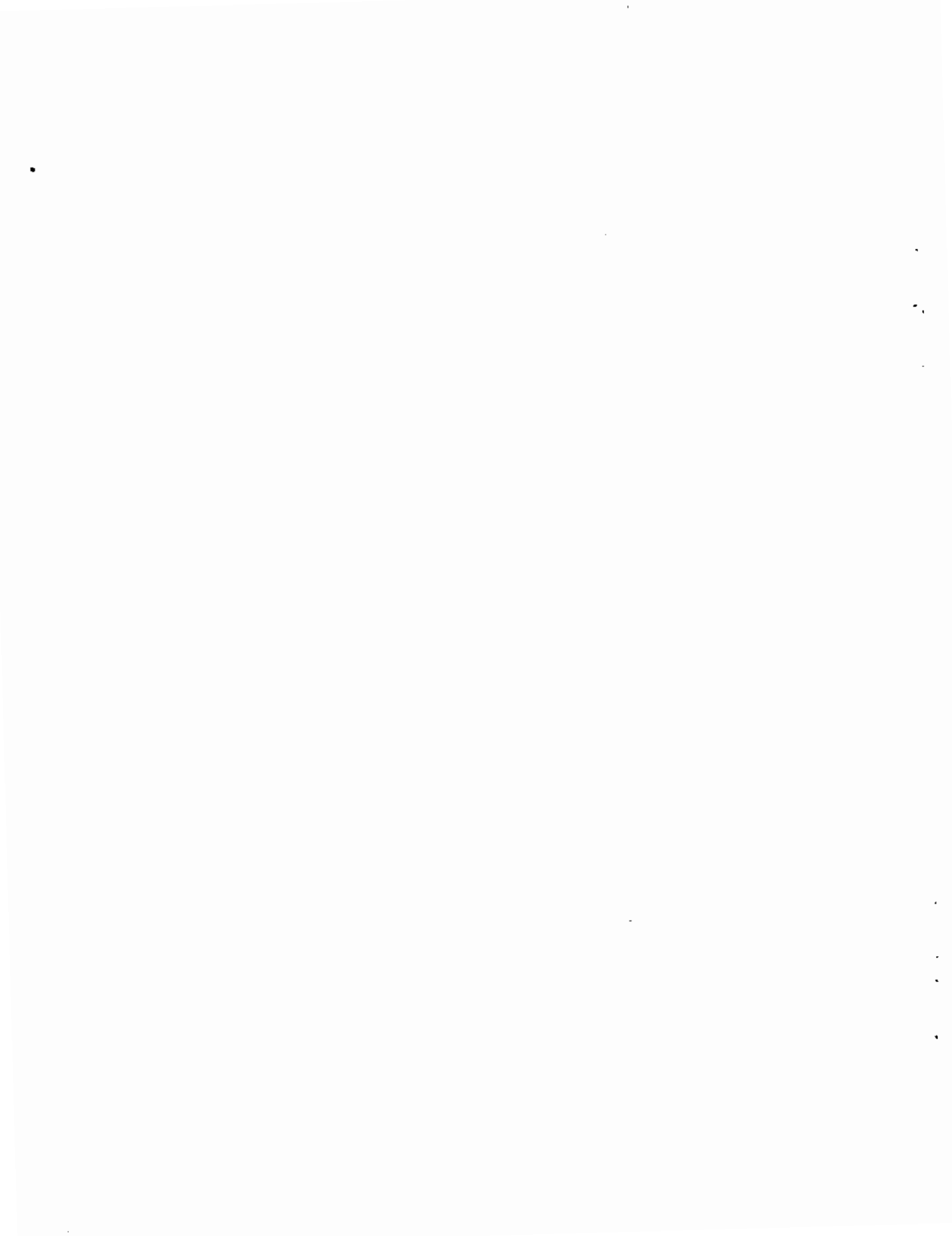
PREFACE

This report is submitted in partial fulfillment of the
contractual obligation for subcontract No. B-96246-A-Q, titled
"Examination of Alternative Catalysts for Biomass Direct
Liquefaction." The report summarizes work performed under this
subcontract during the period 16 April 1981 through 30 June 1982. The
research program was performed in the Chemistry Laboratory of the
Physical Sciences Division under the supervision of Donald L. Ross.
The work was performed by An D. Tran under the technical direction of
Donald Z. Rogers.
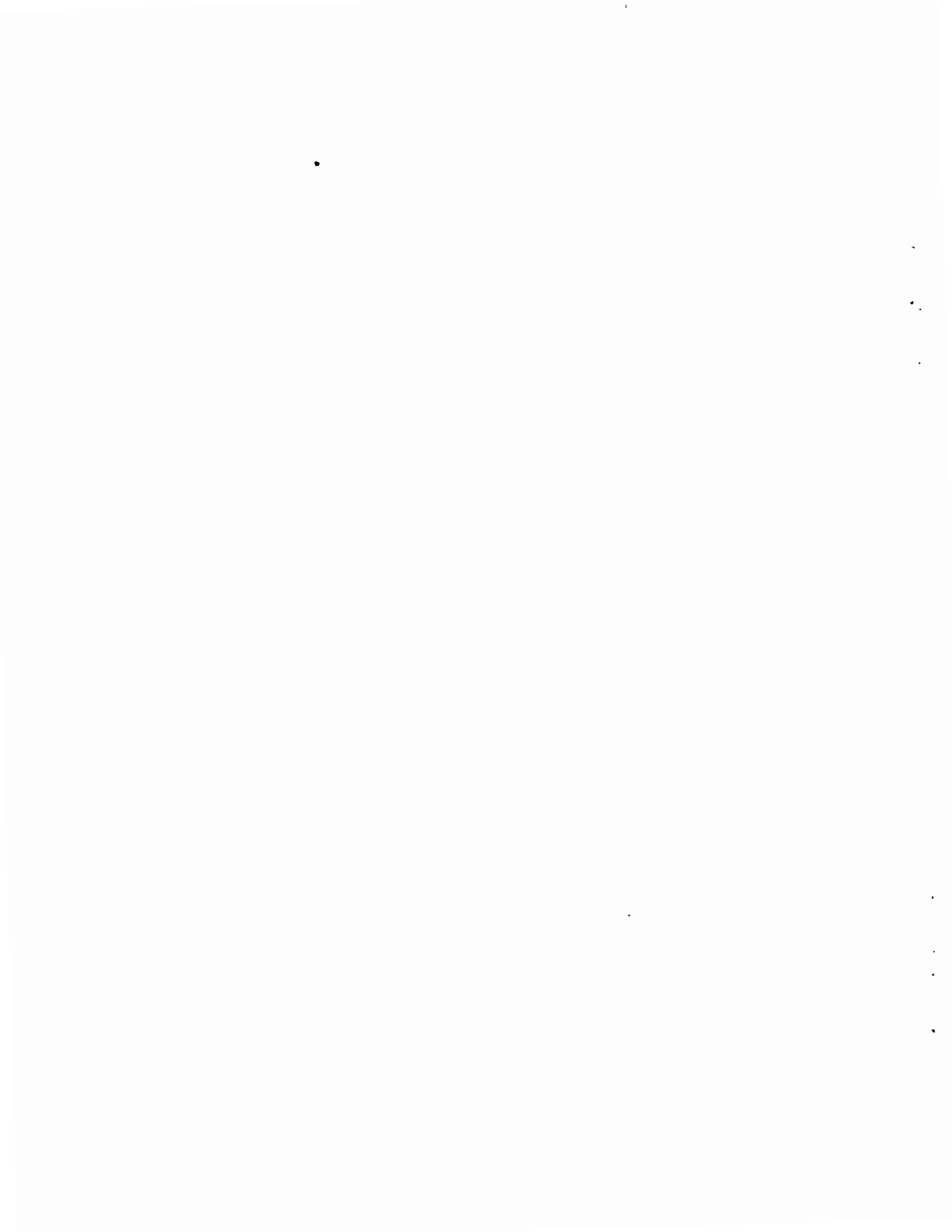
SUMMARY

The goal of the work performed under this contract was to determine the usefulness of water-soluble transition metal salts as catalysts for the direct liquefaction of woodmeal in a carbon monoxide steam process. The work under this contract was divided into two tasks. Task I was a broad spectrum survey of water-soluble transition metal salts as catalysts for direct liquefaction. Task II was an in-depth investigation of salts that showed catalytic activity in Task I.

Fifteen different transition metals were examined in Task I, with several salts containing different ligands being tested in each case. We found that potassium tetracyanonickelate was superior to the other salts tested with respect to the yields of toluene-soluble oils produced. The yields obtained with tetracyanonickelate as catalyst were similar to those obtained with potassium octacyanomolybdate in our earlier work.

Our work in Task II consisted of a more in-depth investigation of the liquefaction of woodmeal with tetracyanonickelate and octacyanomolybdate as catalysts. The role of pH and the reducing gas, and the effect of the ligand on the yields of toluene-soluble products were examined.

The results of these studies have led to the following four conclusions on the mechanism of liquefaction catalysis by water-soluble transition metal salts:

1. Certain salts of nickel and molybdenum are the most
    effective for liquefaction in a carbon monoxide/steam
    process.

2. The metal ligand and the pH of the starting slurry, as
    well as the metal ion, are important in determining the
    yield of toluene-soluble products.

3. The liquefaction of woodmeal by metal salts when carbon
    monoxide is the reducing gas is strongly affected by formate
    chemistry, with significant participation of the metal ion
    as a hydrogenation catalyst.

4. The liquefaction of woodmeal by metal salts when hydrogen
    is the reducing gas is dependent on the action of the metal
    ion as a hydrogenation catalyst, with little or no
    participation by formate.

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I   INTRODUCTION

The goal of the work described in this summary report was to determine which water-soluble salts of transition metals have the potential to act as catalysts for direct liquefaction of biomass in a carbon monoxide/steam process. The efforts under this contract were conducted under the following statement of work.

Task I: Broad Spectrum Survey of Transition Metal Catalysts

Conduct a broad spectrum survey of transition metal salts to determine which metals have the potential to be effective catalysts for direct biomass liquefaction in a carbon monoxide/steam process. Metals to be tested include titanium, vanadium, chromium, cobalt, iron, copper, zinc, niobium, ruthenium, rhenium, cesium, tungsten, lead, and manganese.

Task II: Investigation of Promising Catalysts Found in Task I

Further investigations on catalyst candidates found to be effective in Task I, with specific attention to determining the compounds and oxidation states of the active metals that are most effective as liquefaction catalysts.

Because our results in Task I indicated that the activity of metals as liquefaction catalysts depends critically on the ligand associated with the metal, much of our work was an investigation of the role of the ligand in the liquefaction mechanism. As a part of these

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investigations we determined the effect of starting pH and reducing

gas identity on the liquefaction reaction.

II BACKGROUND

For more than a century, the pyrolysis of wood has been known to produce heavy oils. These oils were usually the undesired by-products in the manufacture of charcoal, which is the main product of simple pyrolysis of wood or other biomass in an inert atmosphere. Periodically during the twentieth century, due to recurrent shortages of petroleum, there has been much interest in the liquefaction of biomass to provide liquid transportation fuels. Before the discovery of the Texas oilfields, destructive distillation of wood to produce methanol was investigated on a pilot plant scale, in particular by the Ford Motor Company. During World War II, there were extensive efforts to produce ethanol from biomass. Although the wartime interest was mostly negated by the discovery of the Mid-East oilfields, the Arab oil embargo of 1973 precipitated a dramatic revival of interest and effort in research on direct liquefaction of biomass.

It was in this context that a group led by Appell at the Pittsburgh Energy Research Center found that high yields of heavy oils could be obtained from biomass liquefaction with 5% sodium carbonate as catalyst and carbon monoxide as reducing agent.[1] During the period of 1974 to 1976 a process development unit (PDU) was constructed at Albany, Oregon, to develop the work of Appell into a continuous process. Although beset by initial design and technical problems of the original facility design, Rust Engineering has recently succeeded in producing several barrels of purely wood-derived oil in the facility.[2]

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A program was developed in support of the PDU facility that included Battelle Pacific Northwest Laboratory (PNL), Lawrence Berkeley Laboratory (LBL), and SRI International (SRI) as contractors. PNL has provided analytical support to the facility, and in addition has also undertaken extensive investigations into process parameters, including catalyst selection and function. LBL initially contracted to provide technical evaluation and monitoring services, and later began an experimental program. LBL has now completed construction of a bench-scale continuous flow reactor that is being used to provide information on process variables in a continuous flow biomass liquefaction process.[3]

The Energy Center of SRI conducted a major study ("Mission Analysis for The Federal Fuels From Biomass Program") on the feasibility and projected market penetration of biomass derived fuels.[4] Later SRI began an experimental program to investigate the basic chemistry and mechanisms involved in direct biomass liquefaction. SRI's experimental program comprised two sequential projects. The results of the first project have been reported;[5] this report is a summary of the results of the second project. The history of the Department of Energy program of research in direct liquefaction and recent advances in the area of liquefaction technology are given in a recent review by LBL.[6]

In the initial stages of work on the first project, we were examining the use of concentrated solutions of base with carbon monoxide for biomass liquefaction. Potassium hydroxide was a very effective base; liquefaction of woodmeal with $KOH/H_2O/CO$ gave a 28%

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yield of toluene-soluble heavy oils containing 19% oxygen. We found
that if the water layer from this liquefaction was neutralized, it was
an equally effective medium for subsequent woodmeal liquefaction, even
though it was nearly neutral (pH 5). Analysis of this water layer
showed it to contain eight metal ion species, representing all the
elements in the autoclave alloy, presumably leached from the autoclave
by the strong alkali.

Although formate was undoubtedly present in the neutralized
water, we hypothesized that the metal ions might also be effective
catalysts in this neutral liquefaction. Because molybdenum was by far
the most abundant metal species (1000 ppm), we chose an appropriate
water-soluble salt, sodium molybdate, to test this hypothesis. We
found that liquefaction of woodmeal with sodium molybdate at a
molybdenum concentration of 1000 ppm in water at pH 5 under carbon
monoxide gave a 36% yield of toluene-soluble products. We then
performed a detailed investigation of the use of various molybdenum
salts as liquefaction catalysts, an account of which is given in our
previous summary report.[5]

Low valent molybdenum salts that were tested showed no activity
as catalysts. These included molybdenum hexacarbonyl and other,
charged carbonyl complexes. Potassium octayanomolybdate, in which the
molybdenum is in a +4 oxidation state, was the most active catalyst
found, giving yields of toluene-soluble products as high as 42%.
While the molybdate and octacyanomolybdate catalysts could be recycled
to some extent, there was a significant loss of activity on recycle.
Possible contributions from formate chemistry were neither excluded

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nor demonstrated.

The technical background that is most relevant to our work is that on the liquefaction of biomass using metal catalysts. Catalytic hydrogenation of biomass or biomass components such as lignin, either by classical, heterogeneous hydrogenation catalysts, or by impregnation of the biomass with metal salts, has been of interest for over fifty years. In 1931 the hydrogenation of biomass catalyzed by common transition metal hydroxides, nickel formate, ammonium molybdate, and ammonium chromate were reported,[7] and in 1931 a second report appeared on the hydrogenation of sawdust impregnated with hydroxides of copper, cobalt, and nickel, sulfides of cobalt, nickel, and iron, molybdic acid, and zinc chloride.[8]

Hydrogenation of biomass over metal oxides and sulfides has been investigated extensively. Heinemann has reported the liquefaction of sugar cane residues over molybdenum oxide and molybdenum sulfide,[9] and the hydrotreating of lignin over iron oxide catalysts was investigated in-depth by Japanese workers in collaboration with Crown-Zellerbach Corp.[10] Other major contributors to the study of metal oxide catalysts include Kashima,[11,12] Hibbert and coworkers,[13-16] and Hachihama.[17-19] Various forms of nickel catalysts[20-22] including Raney nickel[23-25] have been reported to be effective catalysts for biomass hydrogenation. Carbonyls of cobalt, nickel, and iron have also been investigated.[26-29]

This report describes the results of our investigation of direct liquefaction of woodmeal in a carbon monoxide/steam process using water-soluble transition metal salts as catalysts. Also we report our

investigations on the possible role of formate in metal catalyzed liquefactions, and vice-versa. Our work differs from that referenced above in that our process involves simple addition of a water-soluble salt to a reaction mixture consisting only of biomass, water, and the reducing gas. Thus the catalyst is present as an aqueous solution, and not as a suspended solid. An additional difference is the use of carbon monoxide instead of hydrogen as the reducing medium.

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III RESULTS AND DISCUSSION

Experimental Procedure

The standard autoclave procedure used for all liquefaction runs was as follows. In all reactions reported here, 5 grams Douglas fir woodmeal, 15 ml water, and 1.5 millimoles of the catalyst were used. The autoclave (a standard 300-ml 316 stainless steel model manufactured by Autoclave Engineers) was charged with the desired biomass, water, and catalyst, and sealed in accordance with the manufacturer's instructions, except that a copper gasket was used in place of the standard stainless steel fitting. (The copper gasket is inert to the non-corrosive environments under investigation, and allows the autoclave to be more easily sealed.) The mixture was stirred slowly while the vessel was pressurized to 1000 psig with nitrogen and checked for leaks.

After the nitrogen was vented, the vessel was purged with 600 psig of the reaction gas, and charged with the desired pressure of the reaction gas. The magnetic stirrer was then set for a rate of 1500 rpm and the external furnace started. Internal temperature of the reaction vessel was continuously recorded and at appropriate times the vessel pressure noted. The standard conditions for all experiments reported, unless otherwise noted, were a reaction temperature of $350^{\circ}C$ for 45 minutes, with a beginning pressure of 600 psig.

After the vessel had been at the desired reaction temperature for the appropriate time, the external furnace was removed and the reaction vessel cooled with an external fan. In some cases, after the

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final pressure at room temperature was recorded, a sample of the off gases was collected and analyzed by gas phase chromatography. The remaining gases were then vented and the autoclave opened. The aqueous fraction of the product was removed by pipet. The aqueous fractions were not analyzed. The nonwater-soluble materials were collected by washing the autoclave surfaces with 200 ml toluene.

The resulting mixture was then refluxed ($115^{\circ}C$) for one hour under nitrogen atmosphere with azeotropic removal of water. The amounts of water removed were too small to entrain any significant amounts of organic products. After cooling to room temperature, the mixture was filtered by vacuum to yield the toluene-insoluble fraction as a brownish-black solid. The toluene was removed from the filtrate in vacuo to give the toluene-soluble product. In several cases the toluene solvent was examined for low molecular weight products that might have been lost by this procedure; no such light products were found.

In several cases experiments were repeated to determine the reproducibility of the results. In every case yields were reproducible to within 3% of their own value, e.g., a yield of 40% has a possible range of values from 39% to 41%.

Task I: Broad Spectrum Survey

We tested water-soluble salts of the fifteen transition metals proposed in Task I for catalytic activity in direct liquefaction in a carbon monoxide/steam process. For each metal examined we tested several different salts containing different ligands. The highest

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yield of toluene-soluble products obtained for each metal are shown in Table 1. (Results with sodium molybdate and sodium carbonate are shown at the bottom of Table 1 for comparison.) In each case the other salts of the metal gave lower yields than the salt shown. Reactions giving lower yields are reported in Table 2. All experiments were run at 350°C for 45 minutes unless otherwise indicated.

Of the fifteen metals tested, eight (cobalt, chromium, cesium, iron, manganese, nickel, ruthenium, and rhenium) showed some activity as catalysts, giving yields of toluene-soluble products of 30% or greater. Because of their high cost, ruthenium and rhenium are not likely to be of practical interest, but they are of scientific interest and were tested for completeness. With the exception of ruthenium oxide and rhenium carbonyl, all the effective catalysts gave materials with oxygen contents of 11% to 17%, with molar H/C ratios of 1.1 to 1.3. Of these eight effective catalysts, potassium tetracyanonickelate was the best, giving yields (42%) of toluene-soluble products comparable to those obtained with potassium octacyanomolybdate.

Results in Task I also showed that the ligand on the metal plays an important role in determining the catalytic effect of transition metal salts. The effect of ligand on the catalytic activity of cobalt, chromium, iron, manganese, and nickel is shown in Table 2. In each case the best yield of toluene-soluble products was obtained when the the ligand was either cyanide or oxygen. The results of Run 8 (Table 2) also indicated that the pH of the starting slurry was also

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Table 1

ACTIVITIES OF TRANSITION METAL SALTS IN DIRECT LIQUEFACTION

Run	Catalyst	Toluene-soluble Oil				Toluene-insoluble Solids			
		Wt%[a]	C%[b]	O%[c]	H/C[d]	Wt%[a]	C%[b]	O%[c]	H/C[d]
14	$K_3Fe(CN)_6$	30	48	12	1.2	12	15	32	1.1
62	$K_2CO(CN)_6$	35	55	13	1.2	10	70	23	0.7
52	$K_2Ni(CN)_4$	42	66	12	1.3	8.	10	29	1.1
17	$Cu(OAc)_2$	0	--	--	--	46	71	20	0.7
4	$PbSO_4$	8	11	24	1.2	48	66	30	0.7
66	$K_2Cr(CN)_6$	35	58	11	1.1	16	69	23	0.8
9	Na_2WO_4	17	25	21	1.2	23	35	22	0.8
10	$KMnO_4$	30	46	17	1.1	9	12	36	0.8
39	RuO_3	45	65	20	1.4	3	2.	54	1.0
40	$Re_2(CO)_9$	36	47	30	1.1	9	11	36	0.8
32	$Na_2Ti_3O_7$	22	32	23	1.2	44	55	35	0.8
42	CsF	35	56	12	1.2	10	15	78	0.9
41	$NbSe_2$	23	32	26	1.2	11	14	32	1.0
43	ZnF_2	9	12	23	1.1	38	56	24	0.8
33	$NaVO_3$	26	36	25	1.2	20	36	25	1.2
	Na_2MoO_4	36	56	12	1.2	12	14	39	0.7
5	Na_2CO_3	29	44	19	1.1	15	26	13	0.8

a. Weight of product as a percentage of dry feed.
b. Carbon recovered in product as a percentage of carbon in dry feed.
c. Weight percent by difference.
d. Molar ratio.

Table 2
EFFECT OF LIGAND ON THE CATALYTIC ACTIVITY
OF TRANSITION METALS

Run	Catalyst	Toluene-soluble Oils				Toluene-insoluble Solids			
		$Wt\%^a$	$C\%^b$	$O\%^c$	H/C^d	$Wt\%^a$	$C\%^b$	$O\%^c$	H/C^d
14	$K_3Fe(CN)_6$	30	48	12	1.2	12	12	15	1.1
19	$Fe(NO_3)_3$	15	23	19	1.2	26	40	20	0.9
25	$FeCl_2$	1	1	23	1.2	42	63	23	0.7
52	$K_2Ni(CN)_4$	42	66	12	1.3	8	10	29	1.1
28	$Ni(OAc)_2$	13	15	23	1.2	32	52	16	0.8
16	$Ni(NO_3)_2$	9	14	19	1.1	30	48	17	0.8
29	$NiCl_2$	0	--	--	--	47	69	25	0.7
20	$NiSO_4$	3	4.	19	1.2	36	54	22	0.7
62	$K_2Co(CN)_6$	35	55	13	1.2	10	70	23	0.7
15	$Co(OAc)_2$	8	12	22	1.2	33	50	21	0.8
26	$Co(NO_3)_2$	2	3	18	1.2	46	71	19	0.8
27	$Co(Cl)_2$	0	--	--	--	44	66	22	0.7
66	$K_2Cr(CN)_6$	35	58	11	1.1	16	69	23	0.8
7	$Na_2Cr_2O_7$	22	33	20	1.2	27	41	22	0.8
8	$Na_2Cr_2O_7$ (and then KOH to pH 6.5)	29	42	21	1.1	11	15	29	0.8
10	$KMnO_4$	30	46	17	1.1	9	12	36	0.8
18	$Mn(OAc)_2$	9	13	21	1.1	32	49	20	0.8
21	$MnCl_2$	2	20	19	1.2	40	62	20	0.7
22	$MnSO_4$	2	2	20	1.2	42	66	19	0.8

a. Weight of product as a percentage of dry feed.
b. Carbon recovered in product as a percentage of carbon in dry feed.
c. Weight percent by difference.
d. Molar ratio.

important in determining the result of the liquefaction. (Additional data on the effect of pH is shown in Table 4.)

We also tested several of the catalysts at temperatures lower than 350°C. However, potassium permanganate, potassium dichromate, and potassium ferricyanide were all totally ineffective as catalysts for liquefaction at 250°C or 300°C. This caused us to reexamine our previous results with potassium octacyanomolybdate at temperatures below 350°C. All our attempts to reproduce these results were unsuccessful. Our earlier, erroneous results with the octacyano-molybdate catalyst at 250°C appear to have been due to poor accuracy of the temperature control apparatus. This deficiency was corrected before the current work began by aquisition of an Autoclave Engineers temperature controller specifically designed for use with the autoclave system. It now appears that a temperature of 350°C is required for efficient liquefaction no matter what catalyst is used.

At this point in our work we had completed the survey of the transition metal salts. We then turned our attention to a more in depth investigation of the two most promising catalysts, potassium tetracyanonickelate and potassium octacyanomolybdate. Because we had determined that the cyanide complexes of these metals were the most effective catalysts, we investigated in Task II the role of the cyanide ligand, the role of pH, and the relative importance of the metal ion versus the ligand in catalyzing biomass liquefaction.

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Task II: In-Depth Investigation

The seemingly unique activity of cyanide and oxyanion complexes
of molybdenum, nickel, and iron made us suspicious that at least part
of their catalytic activity could be attributed to in situ formation
of formate, which could act as a hydride donor for the hydrogenation
of the biomass in the usual fashion. Cyanide could be hydrolyzed
directly to formate, while the oxyanion complexes might be basic
enough under the reacion conditions to form formate by reaction with
carbon monoxide.

To test this hypothesis we made blank runs $(350^{o}C$,no biomass)
with potassium formate, potassium tetracyanonickelate, potassium
ferricyanide, and potassium permanganate under our standard
conditions. In each case, evaporation of the water from the reaction
product gave potassium formate as the major product in about 85%
yield. These results strongly supported the suspicion that formate
was involved in the catalytic liquefaction of woodmeal by the
transition metal catalysts.

If the catalytic activity of metal cyanide complexes were due
solely to cyanide itself, then all cyanide complexes should give about
the same results, regardless of the identity of the metal, and formate
itself should be an equally effective catalyst. For this reason we
performed a liquefaction run under standard conditions with potassium
cyanide as catalyst. A comparison of the result with those of metal
cyanide complex catalyzed runs is shown in Table 3. All runs in Table 3
except Run 34 were conducted with 1.5 millimoles of catalyst.

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Table 3

CYANIDE SALTS AS LIQUEFACTION CATALYSTS

| Run	Catalyst	Toluene-Soluble Oils					Toluene-Insoluble Solids			
		Wt%[a]	C%[b]	O%[c]	H/C[d]		Wt%[a]	C%[b]	O%[c]	H/C[d]
	$K_4Mo(CN)_8$	42	66	9.6	1.3		5.0	5.0	48	1.1
52	$K_2Ni(CN)_4$	42	66	12	1.3		8.0	10	29	1.1
62	$K_2Co(CN)_6$	35	55	13	1.2		10	70	23	0.7
66	$K_2Cr(CN)_6$	35	58	11	1.1		16	69	23	0.8
14	$K_3Fe(CN)_6$	30	48	12	1.2		12	12	15	1.1
34	KCN (5 mmol)	34	53	13	1.3		6	8	22	1.2

a. Weight of product as a percentage of dry feed.
b. Carbon recovered in product as a percentage of carbon in dry feed.
c. Weight percent by difference.
d. Molar ratio.

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The yield of toluene-soluble products obtained with potassium cyanide was very similar to those obtained with cobalt, chromium, and iron cyanide complexes as catalysts. However, runs with tetracyanonickelate and octacyanomolybdate as catalysts gave clearly higher yields than potassium cyanide. Because various forms of nickel and molybdenum are well known for the their ability to act as hydrogenation catalysts, it seemed likely that in these two cases the metal was in fact contributing to the liquefaction reaction. We therefore turned our attention to a more detailed study of these two metals as catalysts for biomass liquefaction.

To help separate the effect of the derived formate and the metal ion, we performed a series of experiments in which the reducing gas was varied from carbon monoxide to mixtures of hydrogen and carbon monoxide and finally to pure hydrogen. The catalysts selected for these runs were potassium formate, potassium tetracyanonickelate, and potassium octacyanomolybdate. Because the catalytic regeneration of formate requires the reaction of hydroxide with carbon monoxide, we expected that in a hydrogen atmosphere formate would not be an effective liquefaction catalyst. Metal ions, however, would be expected to be effective catalysts in hydrogen, because they can act both as water gas shift catalysts to produce carbon monoxide and as direct hydrogenation catalysts. Therefore, comparing the yields obtained with metal complexes in carbon monoxide and those obtained with metal complexes in hydrogen should provide an indication of the relative contributions of catalysis by formate and catalysis by the metal ion in biomass liquefaction.

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We also suspected from our previous work that the yield of toluene-soluble products in these reactions would depend strongly on the initial pH of the woodmeal slurry. Therefore we determined a "pH profile" (a plot of yield of toluene-soluble products versus initial pH) for these reactions in carbon monoxide and hydrogen atmospheres. Although the initial pH of the slurry is not equivalent to the actual hydrogen ion activity at the reaction temperature, the initial pH should serve as a relative measure of these reactivities. For potassium formate and potassium octacyanomolybdate the pH range examined was from 1 to 12; because tetracyanonickelate decomposes in strong acids, the range for nickel was restricted to 3 to 12.

The pH profiles for liquefaction in carbon monoxide using potassium octacyanomolybdate and potassium formate are shown in Figure 1. Both catalysts were fully effective at a pH as low as 6, and inactive at pH of 2 or less. Although the formate and the octacyanomolybdate gave profiles with the same shape, significantly higher yields were obtained with the molybdenum salt. The inflection point in both profiles occurs at about the pKa of formate ($pK_a = 3.5$). While it is tempting to attribute the the inflection in the pH profiles to a formate to formic acid transition, there is not sufficient evidence to prove the point. The pH dependence of the potassium tetracyanonickelate showed a similar dependence (Figure 2). Elemental analyses were performed on selected products from these pH dependence studies (Table 4). For all three catalysts the character of the toluene-soluble products was fairly constant over the pH range with respect to oxygen content and molar H/C ratio.

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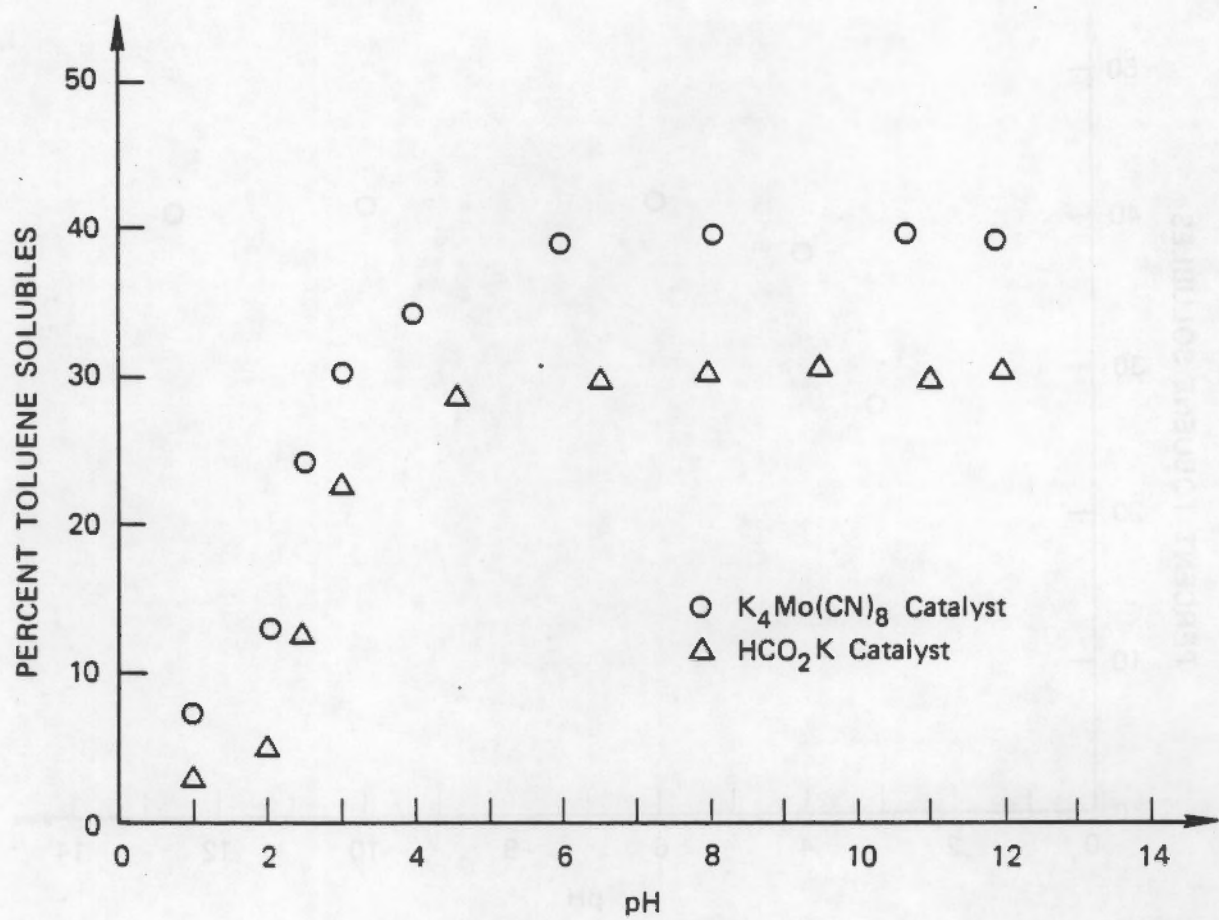
FIGURE 1   pH DEPENDENCE OF WOODMEAL LIQUEFACTION IN A CARBON MONOXIDE ATMOSPHERE

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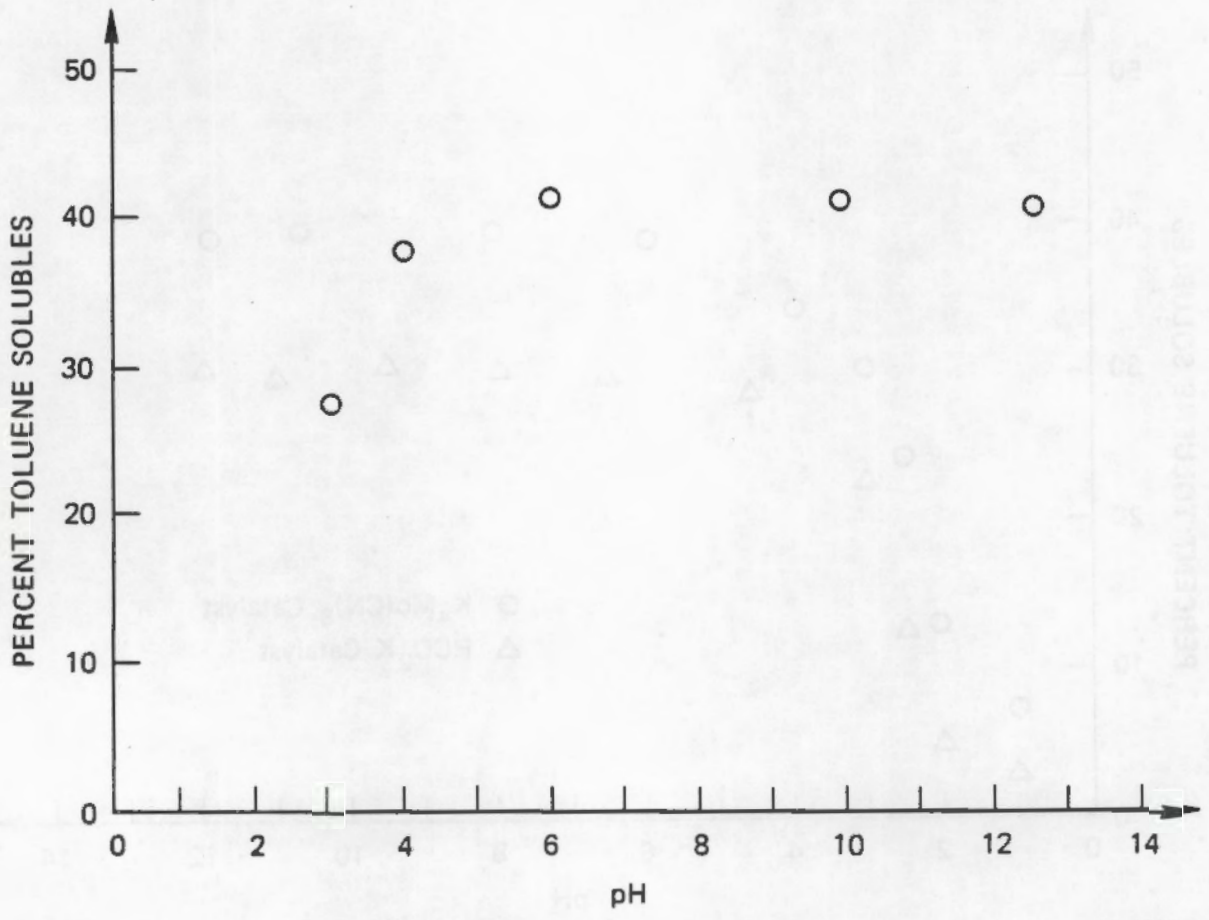
FIGURE 2   pH DEPENDENCE OF TETRACYANONICKELATE CATALYZED LIQUEFACTION
IN A CARBON MONOXIDE ATMOSPHERE

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Table 4

EFFECT OF pH ON TOLUENE-SOLUBLE PRODUCT QUALITY

Run	Catalyst	Toluene-Soluble Oil				Toluene-Insoluble Solid
		$Wt\%^a$	$C\%^b$	$O\%^c$	H/C^d	$Wt\%^a$
	HCO_2K					
75	pH = 2	5	8.3	8.0	1.3	24
77	pH = 3	23	37	8.0	1.3	16
80	pH = 8	30	50	8.0	1.3	15
	$K_4Mo(CN)_8$					
55	pH = 2	13	21	10	1.2	19
64	pH = 3	30	48	11	1.3	14
67	pH = 8	40	69	10	1.3	14
	$K_2Ni(CN)_4$					
69	pH = 3	28	45	8	1.3	14
52	pH = 8	42	69	12	1.2	8.0

a. Weight of product as a percentage of dry feed.
b. Carbon recovered in product as a percentage of carbon in dry feed.
c. Weight percent by difference.
d. Molar ratio.

We also determined the pH dependence of octacyanomolybdate and formate catalyzed liquefactions in a hydrogen atmosphere; these results are shown in Figure 3. Very different results were obtained in this series of experiments than with carbon monoxide. The octacyanomolybdate showed the same pH profile observed in carbon monoxide, although the yield at full activity was somewhat lower in hydrogen (32%). However, for the formate catalyst under hydrogen atmosphere all runs between pH 2 and 10 showed little or no catalyst activity (about 10% yield). Little or no carbon monoxide was produced in the formate runs, while in the octacyanomolybdate runs considerable amounts of carbon monoxide were formed (probably via water-gas shift reactions).

Our results demonstrated that in carbon monoxide formate chemistry is important and perhaps predominant in the liquefaction process. Because carbonate-catalyzed liquefaction is also thought to depend on formate chemistry, we thought it important for other researchers' work, as well as our own, to determine the activity of formate in various mixtures of carbon monoxide and hydrogen, with the goal of determining what compositions of synthesis gas would give full activity with formate catalysts. Because synthesis gas is much cheaper than carbon monoxide, any practical liquefaction process must use synthesis gas. These results are shown in Figures 4 and 5.

Figure 4 shows the yields of toluene-soluble products from formate-catalyzed liquefaction as a function of initial reducing gas composition at a starting pressure of 600 psig. A starting carbon monoxide concentration of 70% is required for full activity. Figure 5

22.
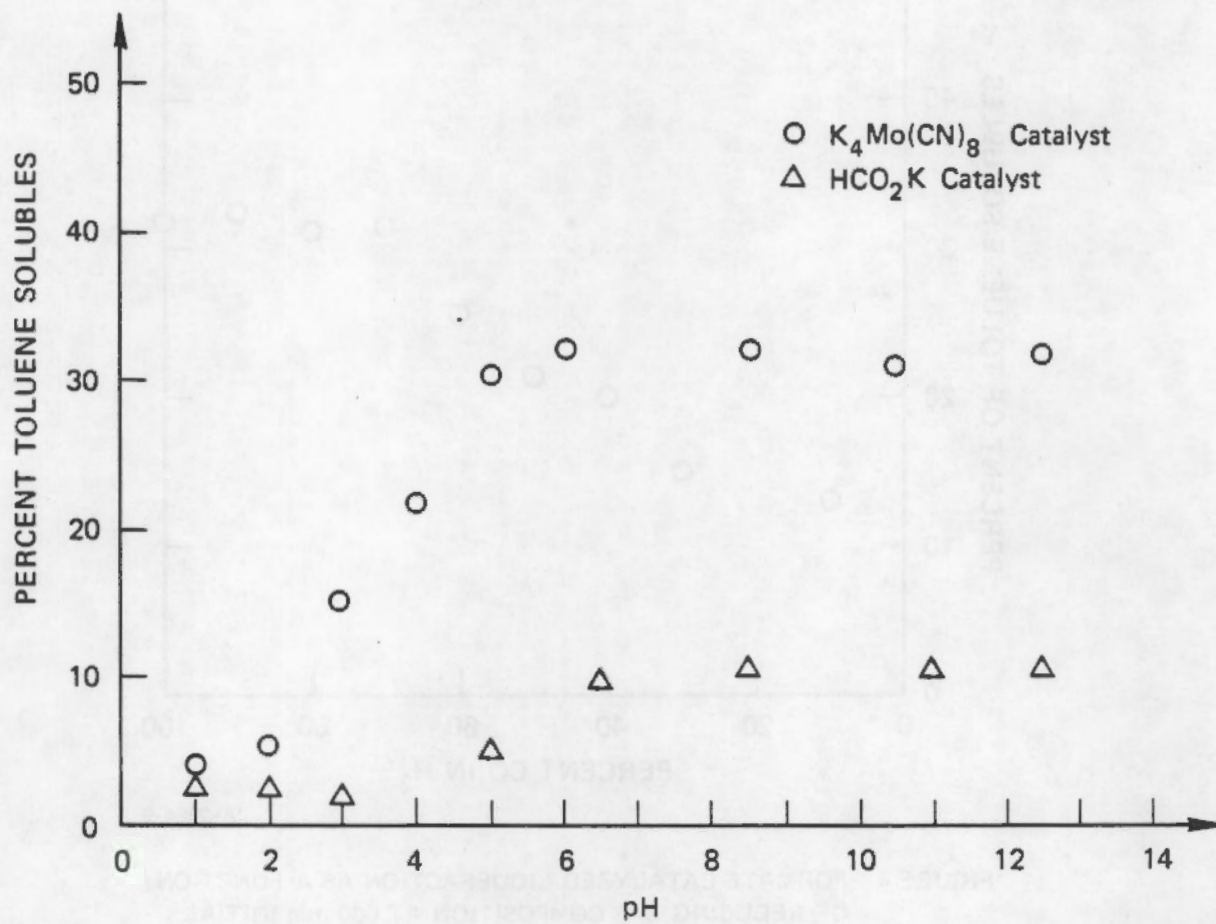
FIGURE 3   pH DEPENDENCE OF WOODMEAL LIQUEFACTION IN A HYDROGEN ATMOSPHERE

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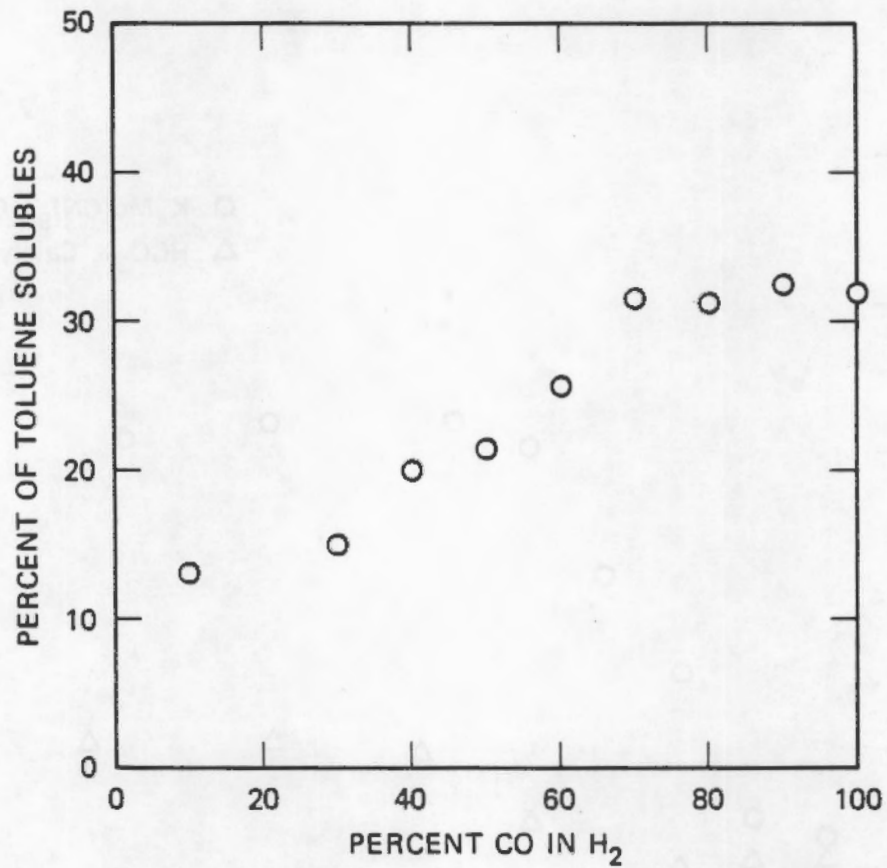
FIGURE 4   FORMATE CATALYZED LIQUEFACTION AS A FUNCTION
OF REDUCING GAS COMPOSITION AT 600 psig INITIAL
PRESSURE

FORMATE CATALYZED LIQUEFACTION AS A FUNCTION OF REDUCING GAS COMPOSITION AT 1000 psig INITIAL PRESSURE

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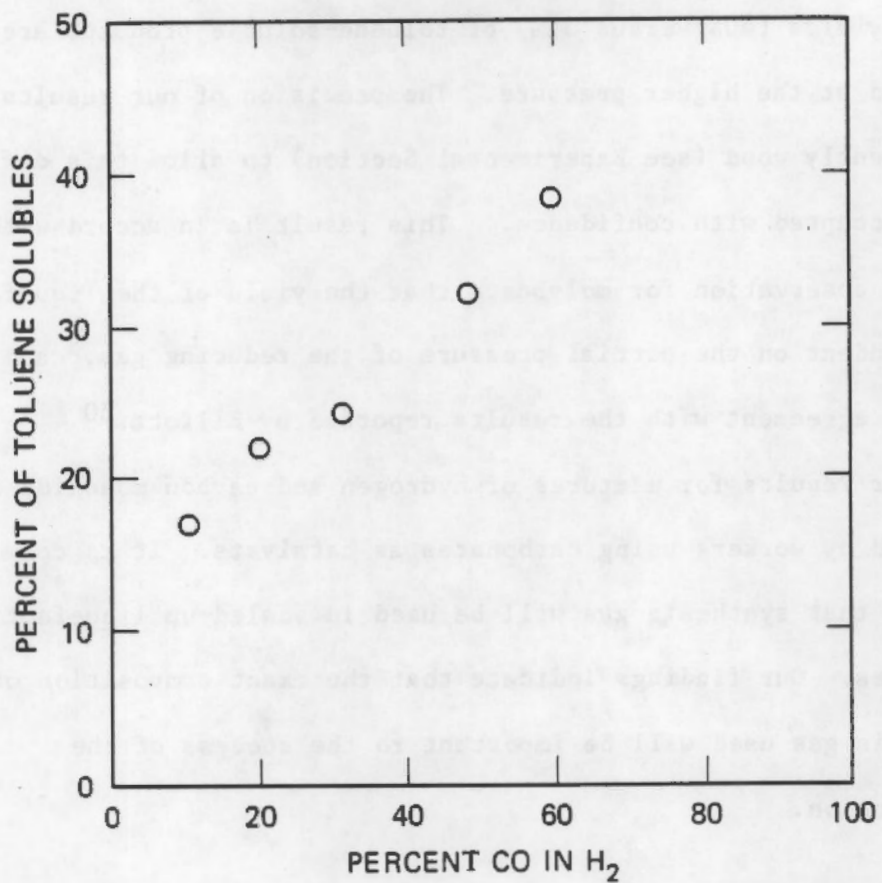
FIGURE 5   FORMATE CATALYZED LIQUEFACTION AS A FUNCTION OF REDUCING GAS COMPOSITION AT 1000 psig INITIAL PRESSURE

shows the results of similar experiments with a starting pressure of 1000 psig reducing gases. When the starting pressure is 1000 psig, full conversion is achieved at 60% carbon monoxide. Also, considerably higher yields (40% versus 32%) of toluene-soluble products are obtained at the higher pressure. The precision of our results is sufficiently good (see Experimental Section) to allow this difference to be accepted with confidence. This result is in accord with our earlier observation for molybdate that the yield of the liquefaction is dependent on the partial pressure of the reducing gas,[5] and is also in agreement with the results reported by Elliott.[30]

Our results for mixtures of hydrogen and carbon monoxide should be noted by workers using carbonates as catalysts. It is commonly assumed that synthesis gas will be used in scaled-up liquefaction processes. Our findings indicate that the exact composition of the synthesis gas used will be important to the success of the liquefaction.

IV CONCLUSIONS

We have now completed a survey study of the water-soluble salts
of all the transition metals that are likely to have utility as
catalysts for direct biomass liquefaction in a carbon monoxide steam
process. Of the fifteen metals that we have examined, certain salts
of molybdenum and nickel are the most effective catalysts, and are the
only species for which some catalytic activity independent of the
ligand can be shown. The most effective forms of the nickel and
molybdenum are cyanide and oxyanion complexes. For nickel the optimum
initial oxidation state is +2; for molybdenum, +4. The oxidation
state of the proximate metal catalysts under the reaction conditions
cannot be determined. The nickel and molybdenum may be forming
colloidal suspensions that act as heterogeneous hydrogenation
catalysts, or they may be forming proximate catalysts that are truly
soluble in the reaction medium.

We have shown that the ligand plays a major role in the
liquefaction reaction in carbon monoxide; the role of the ligand is
determined by its conversion to formate. The pH of the slurry is also
important in determining the outcome of the liquefaction. While the
pH dependence of the liquefaction correlates to the pKa of formate,
the observation of similar pH dependencies in hydrogen atmospheres
requires caution in drawing such a conclusion.

In a hydrogen atmosphere, formate plays little or no role in
determining the outcome of the liquefaction. It is probable that the
metal ion is acting as a hydrogenation catalyst under these

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conditions. At a starting pressure of 600 psig, a gas composition containing at least 70% carbon monoxide is required for full formate activity. Because carbonate catalysts presumably act by forming formate in situ, it is likely that similar results would be observed with carbonate-catalyzed liquefactions. These results bring into question the assumption that hydrogen-rich synthesis gas can be used in a base-catalyzed liquefaction process.

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