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Interim Report

D. C. Elliott
E. G. Baker

March 1986

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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CATALYTIC HYDROTREATING OF BIOMASS LIQUEFACTION PRODUCTS TO PRODUCE HYDROCARBON FUELS

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D. C. Elliott
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Biofuels and Municipal
Waste Technology Division
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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

This report provides interim results of bench-scale testing of catalytic hydrotreatment of both high pressure and pyrolyzate biomass liquefaction products. The goal of this research is to define appropriate operating conditions and catalysts for upgrading biomass liquefaction products to hydrocarbon fuels. Elucidation of the chemistry involved in the processing is a significant portion of the effort.

The results in this report represent the progress during the past four years in this ongoing research project. Successful catalytic hydrotreatment of biomass liquefaction product to a hydrocarbon fuel has been accomplished using typical petroleum hydrotreating catalysts and conditions. The phenolic and polyphenolic wood-derived oil is hydrodeoxygenated and hydrocracked to a gasoline-range hydrocarbon. The product is a mixture of cyclic and aromatic hydrocarbon which is expected to be useful as a high-octane blending agent for gasoline.

The experimentation was performed in both batch-fed and continuous-fed reactor systems. Commercially-available, heterogeneous catalysts were used throughout the research. Processing conditions ranged from 250° to $400^{\circ}C$ at pressures of approximately 2000 psig. Experimental feedstocks and products were analyzed by elemental analysis, distillation, density and viscosity determination, gas chromatography/mass spectrometry and spectrometry methods including infrared and nuclear magnetic resonance.

Among the findings derived from this experimental research, the following appear most important.

- Experiments employing model compounds suggest that alkyl phenolics and naphthols follow similar reaction pathways and have similar kinetics under hydrotreating conditions. A methoxyl substituent on the phenolic ring is thermally unstable and leads to condensation reactions as opposed to hydrogenation reactions.
- Of the catalysts tested, cobalt-molybdenum in the sulfided form has the best combination of high hydrodeoxygenation activity with the least tendency to saturate the aromatic systems, thus producing the largest amount of high octane gasoline components.

- High-pressure liquefaction biomass-derived oil can be directly hydrotreated to a gasoline range hydrocarbon in high yields, but biomass-derived pyrolysis oil cannot be converted to gasoline in high yields under the same conditions.
- Biomass-derived pyrolysis oil can be directly hydrotreated to a gasoline range hydrocarbon in high yields following a low-temperature catalytic treatment. This treatment partially hydrotreats and partially decarboxylates the pyrolyzate so that its thermal stability is sufficiently increased to allow higher temperature catalytic treatment.

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GLOSSARY OF TERMS

Hydrotreating -	chemical treatment with molecular hydrogen, usually catalyzed, for the purpose of removing chemically bound impurities, such as heteroatoms like oxygen, nitrogen and sulfur, from hydrocarbons
Hydrodeoxygenation -	the removal of oxygen from hydrocarbons through hydrotreating
Hydrocracking -	reduction in molecular weight of hydrocarbons by breaking carbon-carbon bonds through catalytic hydrogenation
TR7 Oil -	wood-derived oil produced at the DOE Biomass Liquefaction Experimental Facility formerly at Albany, Oregon by the LBL process
TR12 Oil -	wood-derived oil produced at the DOE Biomass Liquefaction Experimental Facility formerly at Albany, Oregon by the PERC process
TR8D Trap-Out Tray Oil -	wood-derived distillate oil produced through PERC process liquefaction followed by a vacuum distillation, both process steps having been performed at the DOE Biomass Liquefaction Experimental Facility
TR7/12 distillate -	a biomass liquefaction product composed of vacuum distillate oil from both TR7 and TR12
PERC process -	biomass liquefaction process wherein wood feedstock is slurried in recycle oil and reacted at 330-350°C for approximately twenty minutes with carbon monoxide and aqueous alkali to produce a viscous, phenolic tar
LBL process -	biomass liquefaction process wherein wood feedstock is slurried in water, mildly hydrolyzed and then reacted at 330-350°C for approximately twenty minutes with carbon monoxide and aqueous alkali to produce a viscous, phenolic tar
cPs -	centipoise, a measure of viscosity
maf -	moisture and ash free
H/C -	hydrogen to carbon atomic ratio, saturated hydrocarbons have an H/C of 2 or greater, single ring aromatic compounds have an H/C between 1 and 2 depending on the extent of alkylation while condensed aromatics have an H/C of less than 1
coke -	an ill-defined, amorphous, carbonaceous substance

LHSV - liquid hourly space velocity, measured in units of the volume of oil feed per volume of catalyst per hour

PSIG - pounds per square inch gage, 0 psig = 1 atmosphere pressure

Mode I - operation of the continuous-feed catalytic hydrotreater in the extinction cracking mode wherein the wood oil feed is completely converted to gasoline vapor before leaving the reactor

Mode II - operation of the continuous-feed catalytic hydrotreater in the overflow mode wherein unconverted liquid phase wood oil is allowed to spill out of the reactor in conjunction with gasoline product vapor

oxygen rejection - amount of oxygen removed by thermal processing or hydrogenation, measured as a percent of oxygen in the feedstock

INTRODUCTION

This report provides a compilation of the results from the first four years of research on hydrotreating of biomass liquids. Most of this information has been made publicly available previously(1,2,3,4) but this report puts all the earlier information into context. This is an interim report and this research effort is continuing. Just as the development of biomass liquefaction has undergone dramatic forward strides in the past ten years, so will the research on upgrading the liquefaction products in the next five to ten years.

The Department of Energy, Office of Renewable Energy, Biofuels and Municipal Waste Technology Division is presently funding research on upgrading biomass liquefaction products at the Pacific Northwest Laboratory (PNL). The development of upgrading technology was recently highlighted as a major need by an International Energy Agency study on biomass liquefaction.(5) Other research groups are also known to be actively involved in hydrotreating research at the University of Toronto in Canada(6) and at the Chalmers Institute of Technology in Gothenburg, Sweden.(7)

CONCLUSIONS

The recent era of intensive research on biomass liquefaction extends back only seventeen years. Initial goals were to produce a stable liquid fuel. However, more recent emphasis has been to produce transportation fuels (gasoline or diesel) from biomass. The research described in this report provides a basis for continued development of this technology. As a result of this research catalytic hydrotreatment of biomass liquefaction products to a gasoline has been technically demonstrated in a bench-scale continuous processing unit. The specific conclusions presented below cover the development of the chemistry needed for hydrotreatment of both high pressure and pyrolyzate biomass liquefaction products and outlines the important processing knowledge gained by the research.

- Catalyst identity is an important consideration in hydrotreating phenolics. Hydrogenation catalysts such as palladium, copper chromite, cobalt and nickel show activity with nickel being the most active. Major products include benzene, cyclohexane, and cyclohexanone. The dominant product varies with the hydrogenation catalysts. The hydrotreating catalysts cobalt-molybdenum, nickel-molybdenum and nickel-tungsten exhibit some activity when added to the reactor in the oxide form and show a great specificity for hydrodeoxygenation of phenol without saturation of the benzene product. The sulfide form of these catalysts is much more active than the oxide form and, in the case of the cobalt-molybdenum, much of the specificity for hydrodeoxygenation is retained.

- Substitution on the phenolic ring has only marginal effects on the hydrotreating reaction. Alkyl-substitutions on phenol such as methyl, ethyl or dimethyl have little effect on cobalt-molybdenum catalyzed hydrotreating except that the major product is the methyl-, ethyl-, or dimethylbenzene. Naphthols are also hydrodeoxygenated in a manner similar to phenol. However, the methoxy (OCH_3) substituent on the phenol ring is thermally unstable relative to other phenolics tested. The pyrolysis products dominate the product distribution when cobalt-molybdenum is used as the hydrotreating catalyst for guaiacol (methoxyphenol).

- The product from catalytic hydrotreatment of high-pressure biomass liquefaction products confirms the model compound studies. Catalytic processing at 350-400°C and 2000 psig with the sulfided cobalt-molybdenum or nickel-molybdenum catalyst produced a gasoline-like product composed of cyclic and aromatic compounds. Oxygen contents in products were in the range of 0-0.7 weight percent and hydrogen to carbon atomic ratios ranged from 1.5 to 2.0. Low space velocities (less than 0.2 volume of oil/volume of catalyst/hr) were required for complete conversion to gasoline hydrocarbons.

- Biomass flash pyrolyzate cannot be directly hydrotreated to gasoline under the same conditions as the high-pressure liquefaction products due to its thermal instability and resulting carbonization. It can be treated at lower temperature (250-290°C) in the presence of a catalyst (nickel or sulfided cobalt-molybdenum) to produce a stabilized product. Upon catalytic hydrotreatment at more conventional conditions this stabilized product produces a gasoline product like the high-pressure liquefaction oils. The low temperature treatment step requires only low levels of hydrogen but the metal catalyst is necessary to maintain the operation.

BACKGROUND

Previous study has shown that the oil products produced by direct liquefaction or pyrolysis of biomass feedstocks are highly oxygenated. Literature values from 10 to 30 percent oxygen can be found.(8-10) Much of this oxygen is contained in phenolic and guaiacolic components. Although these components might have value in the chemical industry, a general consideration for the upgrading of the product of biomass liquefaction has been the elimination of these components by separation or chemical transformation. To this end we have been testing catalytic hydrotreating as a processing step.

Biomass Liquefaction Processes

In order to comprehend fully the hydrotreating research described in this report, it is necessary to have an understanding of the processing which is used to convert biomass (wood) into crude liquid products. A recent review of these processes (11) shows that two general groups of processes are employed:

1) high-pressure processes with relatively long residence times, and
2) flash pyrolysis processes with relatively higher temperature and short residence times.

The high-pressure processes are epitomized by the operations at U.S. DOE's Biomass Liquefaction Experimental Facility formerly at Albany, Oregon. The Albany Facility design was based on the pioneering work at the Pittsburgh Energy Research (now Technology) Center (PERC).(12) In the liquefaction process (PERC Process) studied at Albany(13) wood chips were ground and mixed with recycled product crude oil. This slurry was pumped to high pressure (3000 psig) and mixed with syngas (carbon monoxide/hydrogen:60/40) and aqueous sodium carbonate. The mixture was then heated at 330-350°C for approximately twenty minutes and then cooled. The pressure was released through a letdown valve and the crude oil product and aqueous by-product were separated by gravity.

A second variation of the high-pressure process was developed through the efforts of researchers at Lawrence Berkeley Laboratory, hence the LBL Process.(14) The LBL Process is the same as the PERC Process except that no oil is recycled and the feed slurry is made with water as the carrier. In order to make a wood flour/water slurry with appropriate properties for high-pressure pumping, an acid hydrolysis pretreatment was developed at LBL. The LBL process was also tested at the Albany facility.

The present U.S. DOE funded effort in high-pressure liquefaction is the development of an extruder-fed reactor system at the University of Arizona.(15) Extruder-feeding is applied to the PERC process in order to increase reactor throughput by increasing the wood-feed concentration and reducing the oil recycle ratio. The reactor system operates in near-plug flow with less back-mixing and thus controls the reaction residence time in a narrower range. Theoretically, the better control of residence time should result in better control of wood oil quality. Other operating parameters of the PERC process remain the same.

The development of the flash pyrolysis type of liquefaction has been underway at the Georgia Tech Research Institute in what is termed an entrained flow pyrolysis reactor system.(16) In the entrained-flow pyrolysis approach, ground wood is carried into the hot (450^o-500^oC) pyrolysis tube by flue gas and is converted to liquid product in 1 to 2 seconds. The liquid product is separated from the by-product gas and char through a series of cyclones, condensers, and demisters. The operation of flash pyrolysis at atmospheric pressure is a great advantage over high-pressure processing. The lack of need of other reagents, such as alkali or reducing gas, also make the process less complex. However, as will be shown in the following section, the product of flash pyrolysis is much different from the high-pressure liquefaction product. Similar chemistry is accomplished by others in fluidized-bed reactors,(17) cyclonic ablative reactors(18) and vacuum pyrolysis systems.(19)

Biomass Liquefaction Products

The two general groups of biomass liquefaction processes result in two general groups of biomass liquefaction products whose properties are summarized in Table 1. The high-pressure processes result in a greater degree of oxygen removal and therefore have a lower affinity for dissolved or emulsified water. As a result of the greater proportion of hydrogen and carbon in the oil, the high-pressure product is also less dense. The presence of low molecular weight oxygenates such as acetic acid, methanol, and light aldehydes and ketones and water, which apparently act like solvents for higher molecular weight materials, cause the flash pyrolysis to be much less viscous.

These two general classes of liquefaction should be used with the knowledge that the product quality is actually a continuum from one extreme to the other. This continuum can be considered as the result of a process severity function wherein temperature, pressure, time at reaction conditions and added reactants or catalysts effect the transformation from the primary pyrolysis products to the more deoxygenated high-pressure products. Transformations along the continuum can be performed in one or more reaction steps. It is the essence of upgrading biomass liquefaction products to proceed along the product continuum past the point represented by the high-pressure product to the complete deoxygenation and production of hydrocarbon liquids. However, it is important to produce useful yields of liquid products and avoid excessive amounts of solid coke or gas production. This trade-off of liquid versus solid and gaseous products is at the heart of all process optimization for biomass liquefaction.

TABLE 1. Properties of Biomass Liquefaction Products

	High-Pressure Liquefaction	Flash Pyrolysis
carbon content	68-81%	56-66%
sulfur & nitrogen content	0.1%	0.1%
oxygen content (maf)	9-25%	27-38%
water in crude	6-25%	24-52%
viscosity, centipoise	2900 @ 40°C - 55,000 @ 60°C	5-59 @ 40°C
density, g/ml	1.10-1.14	1.11-1.23

The chemical components found in biomass liquefaction products include a wide range of oxygenates with very few heteroatom-free hydrocarbons. Due to the low level of sulfur and nitrogen in the biomass feedstock (wood), there is almost no nitrogen or sulfur containing compounds in the biomass oils. Low molecular weight components include acetic acid, glycolic acid, lactic acid, methanol and light aldehydes in the Flash Pyrolysis oils while the High-Pressure Liquefaction products contain almost none of these but do include a noticeable fraction of cyclic ketones. The ketones are both saturated and unsaturated and commonly carry at least one methyl substituent. The character of the phenolics in the two types of products are substantially different. The phenolics in the pyrolysis oils still strongly reflect the lignin structure of the wood. Therefore, little true phenolic is found but mostly methoxyl phenolics. The monomethoxyls (guaiacols) are derived from softwood while the hardwoods give a mix of mono- and dimethoxyl phenolics (syringols) with the syringols the larger fraction. In the pyrolysis oils these guaiacols and syringols often carry a carbonyl-containing side chain or an unsaturated alkyl chain (propenyl). The methoxyl groups are particularly susceptible to thermal scission while the carbonyl and unsaturated side chains provide electron-dense active sites for polymerization. The phenolics in the high-pressure oils are generally alkylated phenols of one type or another. Some guaiacols have been detected as well as dihydroxybenzene (the thermal degradation product of guaiacol) and hydroxynaphthalenes (naphthols). These compounds are more thermally stable and especially so in the absence of aldehydes and acids as is the case in the high-pressure oils.

The information about component structure given in the previous paragraph was determined through the use of gas chromatography/mass spectrometry (GC/MS). However, GC/MS is limited to analysis of only volatile components and, as previous analysis has demonstrated, there is a large fraction of non-volatile components in the biomass liquefaction products.(8) Non-distillable fractions of Albany high-pressure oils have ranged from 1/2 to 1/3 of the total while 1/2 to 2/3 of pyrolysis oils cannot be redistilled after their collection. In the case of the high-pressure oils the bulk of the non-volatile material has been determined to be polyphenolic in character based on spectral analysis and alkaline solubility.(20) Similarly, the higher molecular weight components of the pyrolysis oils are also expected to be oligomer forms of the volatile components which have been identified.

Upgrading Biomass Liquefaction Products

Given the oxygenated character of biomass liquefaction products, the biomass oils as produced could only serve as low grade fuels. Boiler tests with the biomass oils demonstrated their suitability for use as liquid fuels in existing applications.(21,22) However, the need for transportation fuels has been given greater emphasis lately, especially in the European countries.(5) Therefore, a means to upgrade the biomass crude oils to a gasoline or diesel was needed. To accomplish the upgrading, oxygen must be removed from the crude oil and the molecular weight of the material reduced into the gasoline or diesel range.

Our initial upgrading effort at PNL was focused on the high-pressure oils from the Albany facility. We chose hydrotreating as the most direct method to produce high yields of hydrocarbon liquids from the biomass oil. Processing the phenolics of biomass oil to a diesel-equivalent by hydrotreating is theoretically possible. However, it is economically questionable to apply a "deep" hydrogenation process which completely converts a wood-derived oil with an excess of 10 percent oxygen content to a diesel-equivalent.(23) Yet, if hydrogenation could be tailored for hydrogenolysis of carbon-oxygen bonds only, potential exists for an upgrading step which would break down any ethereal linked oligomers as well as split out the oxygen from the oil. This would serve to decrease viscosity through reduction of molecular weight and elimination of polar functional groups while maintaining the aromatic character of the phenolics. While such fine-tuning for hydrodeoxygenation without hydrogenating carbon-carbon bonds has not been a major consideration of hydrotreating research to date, there are indications in the literature that the use of proper catalyst and conditions can favor such processes.

Early Literature on Hydrotreating Oxygenates

Early work on hydrogenation of phenolics was aimed at the production of cyclohexanols. For example, low temperature (<150°C) hydrogenation of phenol to cyclohexanol with nickel(24,25) copper chromite(26) or palladium catalyst(27) was reported. Later studies of nickel catalysts in the presence of catalyst modifiers such as organic base or sulfur demonstrated that the active sites on the catalyst could be affected and result in a changed reaction preference for carbon-oxygen instead of carbon-carbon bonds in phenolics.(28,29) Pines' demonstration that sulfided nickel catalyzes the attack on the carbon-oxygen linkage as opposed to carbon-carbon bonds is particularly significant; however, he experimented with saturated cyclic alcohols not phenols.(30)

These early studies suggest two major considerations in hydrotreating phenolics. First, the operating temperature range can affect the preference for reaction site and low temperature catalytic hydrogenation tends to emphasize carbon-carbon bond reactions versus the preferred carbon-oxygen bond reaction. Second, metal catalysts can be modified from the metallic state in order to emphasize carbon-oxygen bond reaction over carbon-carbon bond reaction.

The production of liquid hydrocarbons through catalytic hydrotreating of biomass-derived liquids is a difficult task owing to the chemically complex nature of the liquid. In all cases, the process must primarily emphasize hydrodeoxygenation with hydrocracking of heavier components. Catalytic hydrodeoxygenation itself, is a relatively new field, mainly a later extrapolation of hydrotreating for sulfur and nitrogen removal from heavy crude oil and coal liquids. Furimsky provides an excellent review of the literature in the field(31); however, he does omit the significant work of Bredenberg et al.(32)

When considering catalytic hydrotreatment of the wide range of components in the biomass-derived liquid product, component-specific hydrogenation provides a key to understanding the processing needs of the whole product. Whereas a reasonable basis for hydrotreating phenolics to aromatics can be determined, the general application of hydrogenation to all biomass liquids is not so reasonable. For instance, the large fraction of organic acids, aldehydes, and ketones with less than a five-carbon backbone found in wood pyrolyzates hold no potential for liquid-hydrocarbon production through hydrogenation. A second example is the difficulty of hydrotreating guaiacol due to its thermal instability. Guaiacol and its family of alkyl-substituted methoxyphenols and dimethoxyphenols are common components in wood-derived liquids and are probably derived from the lignin fraction of the wood. Recent results have shown the guaiacol methoxyl substituent to be relatively, thermally unstable.(32b)

Finding suitable catalysts for biomass-derived liquids upgrading remains the subject of much research. The use of platinum or palladium in relatively high concentrations on alumina has been reported as a catalyst for hydrotreating pine pyrolyzate to some hydrocarbons.(33) There is interest in the use of zeolites; however, early results show only limited conversion of biomass liquids to hydrocarbons.(18,34,35) The more conventional application of hydrodesulfurization catalyst from the petroleum refining industry for hydrodeoxygenation has been studied with phenolics.(32b,32d,32c,36,37) Both molybdenum and tungsten promoted with cobalt or nickel have been used. An important question relative to biomass products which are inherently low in sulfur is the need for sulfiding the oxide catalysts. It has been reported that sulfiding of molybdenum or nickel-molybdenum catalysts decreased the activity for hydrodeoxygenation of naphthol at 225°C.(37)

In summary, there is sufficient previous information to suggest that the oxygenates in biomass liquefaction products can be converted to hydrocarbons through hydrogenation in the presence of a catalyst. This method will not apply specifically to every component type in the biomass liquefaction products and the pyrolysis products in particular contain compounds which may thermally degrade or be converted to gas by catalytic hydrotreating conditions. A number of potential catalytic materials have been identified and there are some indications that control of the operating temperature and modification of certain catalytic metals can lead to greater conversion by hydrodeoxygenation with lesser amounts of hydrogen consumption through saturation of carbon-carbon bonds. Limitation of hydrogen consumption will result in a more economical process.

HYDROTREATING HIGH-PRESSURE LIQUEFACTION OILS

Approach

The experimentation to develop a process to hydrotreat high-pressure liquefaction oils occurred in three stages. Initial tests were made with model compounds in a batch reactor system. The goals of this work were three fold: 1) determine differences in hydrogenation activity of a number of phenolic species, 2) determine differences in activity for a number of catalyst compositions, and 3) briefly survey the conditions at which catalytic hydrotreatment might be attempted. The second stage of our research was the testing in a continuous-feed system with biomass liquefaction product distillates. There were two goals of this stage of the work: 1) demonstrate the continuous-feed reactor system with a low viscosity biomass-derived feedstock as a means to produce hydrocarbon products and 2) verify the extrapolation of the catalyst specificities from the model compounds to biomass-derived products. The third stage of the PNL work was to determine reaction kinetics and product compositions from the catalytic hydrotreatment of biomass liquefaction products. The fixed-bed, continuous-feed reactor system was also used in this third stage of work. Detailed descriptions of the reactor systems are included as an appendix to this report.

Model Compound Experiments

Hydrogenation of phenolics can lead to several products and a wide range of hydrogen consumption results depending on the product mix as shown in Figure 1. The product of choice is the aromatic product which maximizes oxygen removal and minimizes hydrogen consumption. Based on available literature both operating conditions and catalyst composition are significant factors in determining product distribution.

The catalysts chosen for these tests covered a broad range of heterogeneous, supported-metal catalysts. These catalysts are those suggested by earlier successful tests in hydrogenation of phenolic materials. The list, given in Table 2 includes not only hydrogenation catalysts like copper chromite, nickel, palladium and cobalt but also the hydrotreating catalysts developed for the petroleum industry such as the cobalt or nickel-molybdenum or nickel-tungsten catalyst.

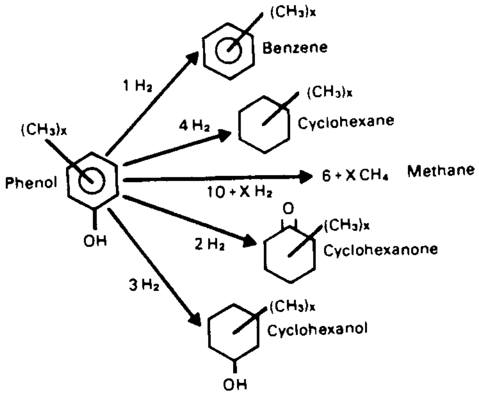

FIGURE 1. Hydrogenation Products from Phenolics

Procedure - The batch reactor described in the appendix was used for these experiments. The catalyst of choice was loaded in the catalyst basket in its tableted or extruded manufactured form. The phenolic feedstock was charged to the reactor and the reactor was sealed. The reactor was purged and then pressurized with hydrogen. The reactor was then heated to reaction temperature, held for the specified time and cooled. The reaction products were analyzed by gas chromatography; no total mass balance was attempted. The reaction products are reported as mass percent concentration in the unconverted phenolic feedstock. Qualitative analysis was the major emphasis of the analysis while the quantitative data is not considered highly precise. The batch nature of the test and the low levels of conversion cause the quantitative data to be less meaningful, while relative changes among the different catalysts is considered more important.

TABLE 2. Catalysts Tested for Hydrodeoxygenation of Phenolics

Catalyst	Manufacturer Number	Manufacturer	Composition
Hydrogenation			
Copper Chromite	G22RS	United Catalysts	33.0% Cu, 27% Cr, 11% Ba
Palladium	Pd0501	Harshaw	0.3% Pd metal
Cobalt	Co0127	Harshaw	39% Co on Kieselguhr, reduced & stabilized
Nickel	Ni1404	Harshaw	68% Ni on alumina/silica, reduced and stabilized
Hydrotreating			
Nickel-tungsten	Ni4301	Harshaw	6% Ni, 19% W
Nickel-molybdenum	HT500	Harshaw	3.5% NiO, 15.5% MoO_3
Cobalt-molybdenum	CoMo0402	Harshaw	3% CoO, 15% MoO_3 on silica/alumina

In a number of cases, the product offgas following the experiment was found to contain very little hydrogen. These experiments were therefore determined to be limited in conversion by the amount of hydrogen available for reaction. These experiments have been noted in Table 3.

Results - The results of hydrogenation of phenol with the different catalysts is presented in Table 3. Operating conditions of temperature and pressure are given for each experiment as well as the analysis of the product components. The major products in all cases were the deoxygenation product, benzene; the hydrogenation product, cyclohexanone; and the combined deoxygenation and hydrogenation product, cyclohexane. Other minor products were also identified and are listed in the table.

Of the hydrogenation catalysts only the nickel and cobalt metal show reasonable specificity for hydrodeoxygenation. In all tests with the copper chromite catalyst the preferred benzene product is produced in lesser quantities than the two saturated products. With palladium a noticeable temperature effect is detected wherein benzene is the preferred product at higher temperature and cyclohexanone is preferred at lower temperature (commercial synthesis of cyclohexanone from phenol has been performed at even lower temperature). The nickel and cobalt metals both show strong hydrodeoxygenation activity with good activity to saturate the aromatic ring as well. Sulfiding the nickel catalyst by treating with hydrogen sulfide (H_2S) results in reduced activity but a greater tendency to saturate the aromatic ring. Hydrocracking of the ring to produce methane (CH_4) and methyl radicals which can methylate the ring is strongly evident with the nickel metal and to a much lesser degree with the cobalt. Sulfiding the nickel appears to eliminate the hydrocracking activity entirely.

The hydrotreating catalysts were initially tested in their oxide forms. In this form they have limited activity but a strong preference for hydrodeoxygenation with little tendency to saturate the aromatic ring. All three catalysts gave comparable results but the nickel-molybdenum and -tungsten catalysts did exhibit some cracking tendency with the formation of cresols. Both a pressure and temperature effect can be seen for the cobalt-molybdenum tests. The cobalt-molybdenum catalyst (CoMo 0402) was tested further in both a prereduced form (by pretreatment with hydrogen) and a sulfided form (by pretreatment with H_2S). The prereduction process destroyed the strong hydrodeoxygenation specificity while increasing its overall

TABLE 3. Hydrogenation of Phenol

Catalyst	Temp. °C*	Initial Hydrogen Pressure psig	Mass Percent Product			
			Cyclohexane	Cyclohexanone	Benzene	Other
Hydrogenation						
CuCr	300**	900	1.8	1.8	0.9	
	400**	900	1.9	1.8	1.6	
	400**	1775	5.2	5.0	1.9	
Pd	300**	900	2.5	8.1	2.0	
	400**	1750	2.7	5.5	7.8	0.9 o-phenylphenol
Co	400	1000	2.5	0	2.6	0.2 CH_4
Ni	400**	1950	7.6(5.7)	0(0)	16.9(11.8)	3.0 (1.9) CH_4 1.8 (7.1) cresols
Ni-H_2S	400	1700	8.0	0	0.4	0.5 cyclohexene 0.7 cyclohexylbenzene
Hydrotreating						
NiMo	400	2000	0.0	0	4.4	2.0 cresols 1.0 diphenylether
NiW	400	900	0	0	1.1	2.8 cresols
	400	1275	0	0	1.8	1.9 diphenylether
CoMo	300	1010	0	0	0	
	400	900	0	0	1.1	
	400	1100	0	0	2.0	
	400	1800	0(0)	0(0)	5.9(2.3)	
	425	2050	0	0	6.0	
CoMo-H_2	400	2050	2.1	6.0	0.5	1.5 cyclohexylphenol
CoMo-H_2S	400**	2000	3.6(0.5)	0(0)	33.8(13.1)	0.4 (0) biphenyl 2.0 (0.2) cyclohexylbenzene

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numbers in parentheses are results with recycle catalyst without regeneration

* one hour at temperature

** hydrogen limited in batch reactor

activity only a little. The sulfided catalyst was greatly activated and maintained most of its specificity for hydrodeoxygenation without saturation of the aromatic ring.

Discussion - It is apparent from reviewing the data in Table 3 that the catalyst composition has a large impact on the product composition of hydrotreating phenol. The sulfided form of the cobalt-molybdenum catalyst stands out as a well-suited catalyst for our needs due to its strong hydrodeoxygenation activity with limited activity for saturation of the aromatic ring. The use of the sulfided CoMo catalyst appears to be preferred for hydrodeoxygenation of phenolics; however, the introduction of sulfur into the system could be a serious drawback. Since no significant amount of sulfur is present in the feedstock, a continuous scheme for sulfiding the catalyst may be required. Chemical incorporation of the sulfur from the catalyst into the product is a potential problem. For these reasons the less specific nickel catalyst may still be the catalyst of choice for hydrodeoxygenation of wood oil.

Long-term catalyst activity cannot be well-judged by batch reactor testing. However, as a first attempt to measure catalyst life, catalyst charges from three experiments were returned to the autoclave for a second test as indicated in Table 3. These tests showed a decreased catalyst activity during the second cycle in each case. The decrease was most noticeable in the case of the sulfided catalyst. No attempt was made to regenerate or resulfide the catalysts between tests.

A typical gas chromatograph of the product from phenol hydrodeoxygenation when catalyzed by sulfided cobalt-molybdenum is shown in Figure 2. As with all the more active catalysts the most abundant products are single-cyclic compounds. However, there are significant quantities of dicyclic compounds as well as traces of tricyclics. We found no cyclohexylphenyl ether and suggest that Haider has misidentified the cyclohexylphenol as evidenced by his mass spectral data.(36) No evidence of cyclohexanol was found in the product with the sulfided CoMo catalyst or most of the other catalysts tested at these conditions. Only traces of cyclohexanol were found in the nickel catalyzed product, and we conclude that cyclohexanol is not a significant intermediate with these catalyst systems at these temperatures.

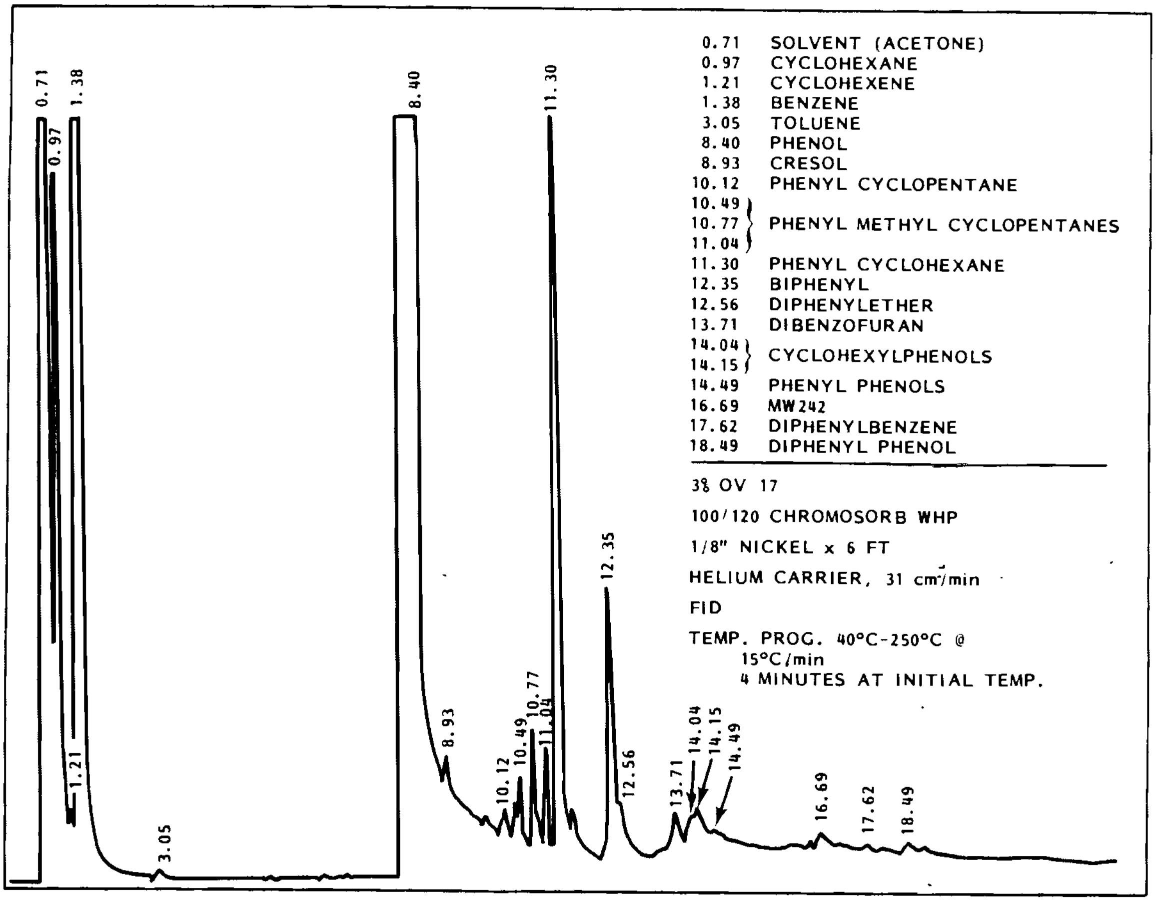

FIGURE 2. Gas Chromatographic Separation of Product from Hydrotreatment of Phenol

Additional Model Compound Experiments

As an extension of model compound catalysis experiments with phenol, alkylated phenols, guaiacol (ortho-methoxyphenol) and a naphthol were also tested. These tests were performed to determine if substitution on the phenolic ring (as is commonly found in wood-derived oil) would affect the pathway or rate of hydrodeoxygenation.

Procedure - These experiments were performed in the batch reactor in a manner similar to that used in the phenol hydrotreating tests. All experiments were performed with cobalt-molybdenum catalyst due to its high specificity for hydrodeoxygenation with minimal saturation as shown with phenol. The sulfided form of the catalyst was not used in these tests due to the difficulty of the sulfiding procedure in the batch system. Adequate comparison can be made between the results in Table 4 and the cobalt-molybdenum catalyzed test at 400°C and 1800 psig listed in Table 3. The feedstocks were Aldrich reagents and were 99+% pure in the cases of phenol, cresol and naphthol and 97% pure or better for the other reagents. No repurification of the feedstocks was attempted in the laboratory. All experiments were performed at 400°C for one hour with an initial hydrogen pressure of 2000 psig.

Results - The experiments demonstrate that the alkylated phenolics and naphthol follow reaction pathways similar to phenol. The identities and quantities of the products are listed in Table 4. The product specificity for deoxygenation without ring saturation remains, but there is substantial evidence of migration of the alkyl substituents. We would expect that conversion of the model compounds would be increased by the use of the sulfided catalyst as was found with phenol.

The results from guaiacol hydrotreatment present a much more complex picture. Demethylation is a highly competitive reaction with this model compound. There is evidence of dimerization and possibly polymerization based on the high viscosity of the product and its dark color. Evidence of high molecular weight material (xanthenes) was also found with gas chromatography - mass spectrometry. It appears that catalytic hydrodeoxygenation was not the major reaction pathway in this experiment.

Discussion - These results suggest that similar kinetics and product distributions should be achieved despite the amount of alkylation of the phenolic rings in the biomass liquefaction product. Also, these experiments give a good indication that the naphthols (hydroxynaphthalenes) found previously in wood-derived oil should also be hydrodeoxygenated by this same hydrotreatment process. However, the experiment with guaiacol indicates that the methoxy-substituted phenolic components may not be adequately treated under the same conditions. In the guaiacol test, the hydrotreated product had a composition similar to that reportedly produced under strict pyrolysis conditions.(32b) Apparently, the pyrolytic pathway was dominant for guaiacol reaction under the conditions used in our catalytic test. By comparison, under pyrolysis conditions at 400°C methylphenol and naphthol have been reported as unreactive(38) while dimethylphenol was found to be unreactive at temperatures as high as 450°C.(39)

These results point out differences caused by substituent functional groups on the phenolic ring and suggest that general extrapolation of hydrotreating results from phenol as a model compound to the complex mixture which is biomass liquefaction oil is tenuous at best.

TABLE 4. Products from Hydrotreatment of Phenolics

Feedstock	Aromatic Product	Saturated Product	Other Products
4-methylphenol	methylbenzene (4.5) benzene (1.0)	methyl cyclohexanone (0.6)	--
3,5-dimethylphenol	dimethylbenzene (5.1)	--	methylphenol (5.0) trimethylphenol (3.1)
p-ethylphenol	ethylbenzene (3.5)	--	phenol (4.6) ethylphenols (20.6) C_1-C_4 phenols* (trace)
2,3,5-trimethylphenol	trimethyl benzene (4.0) C_2+C_3 benzenes* (trace)	--	dimethylphenols (9.0) C_4 phenol* (14.0) C_3 phenol* (3.2)
hydroxynaphthalene	naphthalene (8.7)	tetrahydronaphthalene (4.4) dihydronaphthalene (0.4) hydroxytetrahydronaphthalene (0.7)	C_4 benzene* (0.5)
o-methoxybenzene	methoxybenzene (trace) methylmethoxybenzenes (trace)	--	phenol (20.1) methylphenols (19.1) dimethylphenols (4.6) dihydroxybenzene (15.2) xanthene (trace)

---

1 hr, 400°C, 2000 psig initial H_2 pressure, CoMo catalyst
Values in parentheses are weight percent yield
* C_x preface indicates an X number of carbons attached in various length alkyl substituents

Biomass Liquefaction Product Distillate Hydrotreating

Hydrotreating of biomass liquefaction product distillates was undertaken in a continuous-feed reactor system as a transition stage from the model compound experiments in the batch reactor to whole oil experiments in the continuous-feed reactor. The continuous-feed reactor (as described in detail in the appendix) was required due to the shortcomings of the batch reactor system. These shortcomings included: 1) limited control of the hydrogen partial pressure as the experiment progressed, 2) doubts about the adequacy of the mass transfer among the three phases in the reactor, 3) difficulty in sulfiding the catalyst, and 4) difficulty in interpreting kinetics based on the batch-fed experiments.

The distillate hydrotreating experiments were used as a means of testing the operation of the continuous-feed system and to determine the effect of catalyst composition on true biomass-derived products. The distillate was a low viscosity material which contained little of the high-molecular-weight components known to be present in the whole oil. For these reasons the distillate was expected to pump easily and not plug up the catalyst bed. The low-molecular-weight material would be hydrotreated more easily and there would be less tendency for coke formation.

The catalysts chosen for these experiments were derived from the results of the model compound experiments. The cobalt-molybdenum was chosen as the best for hydrodeoxygenation, the nickel was the best hydrogenation catalyst and the copper-chromite was included as a less active catalyst for comparison. The catalysts used are described in Table 5. The specific catalysts used are those which were available from a manufacturer and are used as representatives of a generic catalyst composition. No determination has been made, for

TABLE 5. Catalysts Used in Hydrotreating Wood-Derived Distillate Oils

Catalyst	Manufacturer No.	Manufacturer	Composition	Form
Cobalt-molybdenum	CoMo0402	Harshaw	3% CoO, 15% MoO_3 on silica/alumina	1/8, 3/16, 1/4 in. pellets
Nickel	Ni1404	Harshaw	68% Ni on proprietary support	1/8" pellet
Copper Chromite	G22RS	United	33% Cu, 27% Cr 11% Ba	1/8" pellet

example, that the CoMo0402 is the best cobalt-molybdenum catalyst for these purposes. These catalysts are all commercially available and were used in their pelletized or extrudate form.

Procedure - For these tests the continuous-feed reactor was used. The catalyst was poured into the reactor and it was sealed and purged. Pretreatment of the catalyst was required for the nickel catalyst (reduction with hydrogen) and for sulfided cobalt-molybdenum tests (reaction with 10% H_2S in hydrogen). After the catalyst bed was ready and preheated to temperature, the flow of hydrogen and then distillate was begun. Products were collected following the condenser. Analysis of the products included elemental analysis, distillation, heat of combustion, infrared spectrophotometry, nuclear magnetic resonance spectrometry, and gas chromatography-mass spectrometry.

The two distillate oils tested initially in the continuous-feed reactor were products from the Albany Biomass Liquefaction Facility. The TR(x) name for the distillates indicates the specific test run wherein the distillates were produced. Details of the specific production runs can be found in Reference 40. A summary of the analyses of the distillates is given in Table 6. The TR8D Trap-Out Tray Oil was produced at Albany in a process scale, flash-distillation column. The TR7/12 distillate was a combined distillate product from several laboratory-scale vacuum distillations performed at PNL.

TABLE 6. Distillate Feedstock Descriptions

Feedstock	percent composition C	H	O	Moisture	Density	H/C Atomic Ratio
TR8D Trap-Out Tray Oil	81.8	8.6	9.7	0.0	1.05	1.25
TR7/12 Distillate	76.2	8.9	14.9	2.3	1.03	
(dry)	(78.0)	(8.8)	(13.2)	(0.0)		(1.34)

Results - The low-viscosity TR8D Trap-Out Oil was used as the common feedstock for a series of comparative catalyst tests. Table 7 contains the relevant operating data and summary product descriptions for these tests. For each of four catalyst tests there are two data subsets which define two sets of operating conditions during the test. These data subsets can provide a little insight into the effects of the different operating parameters on the product quality. For the nickel case and the sulfided cobalt-molybdenum (0402) case the difference in the final product properties is apparently due to a drop in reactor temperature of approximately 60°C. In both cases the oxygen content in the product increased with the decrease in operating temperature. For the nonsulfided cobalt-molybdenum (0402) case a large decrease in the hydrogen feedrate, caused a slight increase in hydrogen incorporation and oxygen removal. In the copper chromite case the product quality drops slightly as an apparent result of the decrease in operating pressure and temperature. It is most important to note that none of these parameter changes had as dramatic effect on the product quality as the choice of catalyst.

Discussion - The product quality and distribution ranges widely with the four different catalyst types tested. As suggested earlier in the model compound studies, the nickel catalyst is very active for hydrotreating wood-derived oil. As shown in Table 7, the product from the nickel-catalyzed test

TABLE 7. Hydrotreating Catalyst Comparative Tests with Wood Oil Distillates

	TR8D Trap-Out Tray Oil								TR7/12
Experimental Parameters	Nickel		Sulfided CoMo		CoMo		CuCr		Sulfided CoMo
	a	b	a	b	a	b	a	b	
Temperature, °C	347	284	358	300	355	343	327	315	344
Pressure, psig	2314	2302	2023	2022	2022	2010	2086	1920	1965
Oil Feed Rate, ml/hr	186	186	225	277	240	240	672	246	342
Hydrogen Feed Rate, l/hr	271	271	206	206	162	30	305	305	137
LHSV, vol. oil/vol. cat./hr	0.22	0.22	0.23	0.29	0.27	0.27	0.75	0.27	0.38
Experimental Results									
Hydrogen Consumption l/l oil	695		276		96		--		178
Hydrogen Consumption, SCF/bbl	3900		1500		540		--		999
Carbon Conversion, wt%									
to Gas	5.3		0.4		0.4		0.2		1.0
to Coke on Catalyst	18.9		10.9		13.1		8.3		19
to Liquid Product	74		87		85.5		87.5		70
Overall Carbon Balance	98%		98%		99%		96%		90%
H/C Ratio of Product	1.95	2.08	1.62	1.44	1.30	1.33	1.46	1.41	1.72
0 Content of Product, wt%	1.1	1.5	2.0	2.4	7.7	7.3	8.5	9.5	2.2

a and b indicate two subsets of data from one continuous test. Operating conditions were changed during the runs as presented in the table. These parameter changes had only minor effects on the product quality as indicated in the table.

is low in oxygen and is highly saturated with hydrogen as suggested by the hydrogen to carbon (H/C) ratio of approximately 2. The relatively high carbon conversion to gas (5.3 wt% versus 1 or less for other tests) results from a high rate of methane formation at the beginning of the experiment which steadily decreased to almost nil by the end of the experiment. This variation in combination with the coke buildup on the catalyst (Table 7 indicates 18.9% carbon conversion to coke on the catalyst) may indicate a deactivation of the catalyst. The effect of any such deactivation on liquid product quality is minor. The product is a light yellow clear liquid whose infrared spectrum shows strong alkane bands (2900-3000 cm^{-1}) with nearly total elimination of hydroxyl (3400 cm^{-1}), carbonyl (1700 cm^{-1}), and aromatic bands (3000-3100 and 1600cm^{-1}). Infrared spectra of products and feedstocks are given in Figure 3. The proton nuclear magnetic resonance spectrum supports this analysis (Figure 4) wherein the primary components identified are methyl groups and methylene groups as five-, six-, and seven membered rings. Lesser amounts of aromatics (possibly including phenolics) and methyl substituents on aromatics were also identified. The definitive analysis of gas chromatograph/mass spectrometry also correlates well with these analyses. As shown in Table 8, the primary components produced in the hydrotreatment of the TR8D Trap-Out Tray Oil with nickel catalyst are alkyl cyclohexane hydrocarbons of the gasoline boiling range. The polycyclic hydrocarbons are believed to be remnants of the anthracene oil used as start-up slurry medium in the liquefaction facility.

The sulfided cobalt-molybdenum (0402) catalyst is nearly as efficient in oxygen removal as the nickel catalyst, as indicated by the low oxygen content of the product; but hydrogen consumption is much less apparently due to the lesser degree of saturation of the aromatic compounds. Also, methane production was almost nil. The lesser degree of saturation is shown by the lower hydrogen to carbon ratio in Table 7, the stronger aromatic IR bands in Figure 3, and the large number of benzene and other aromatic components identified in the GC/MS chromatograph in Table 8.

The other two catalysts were much less active. The copper chromite catalyzed some hydrogenation as suggested by the increase in hydrogen to carbon ratio from feedstock to product, but almost no deoxygenation occurred.

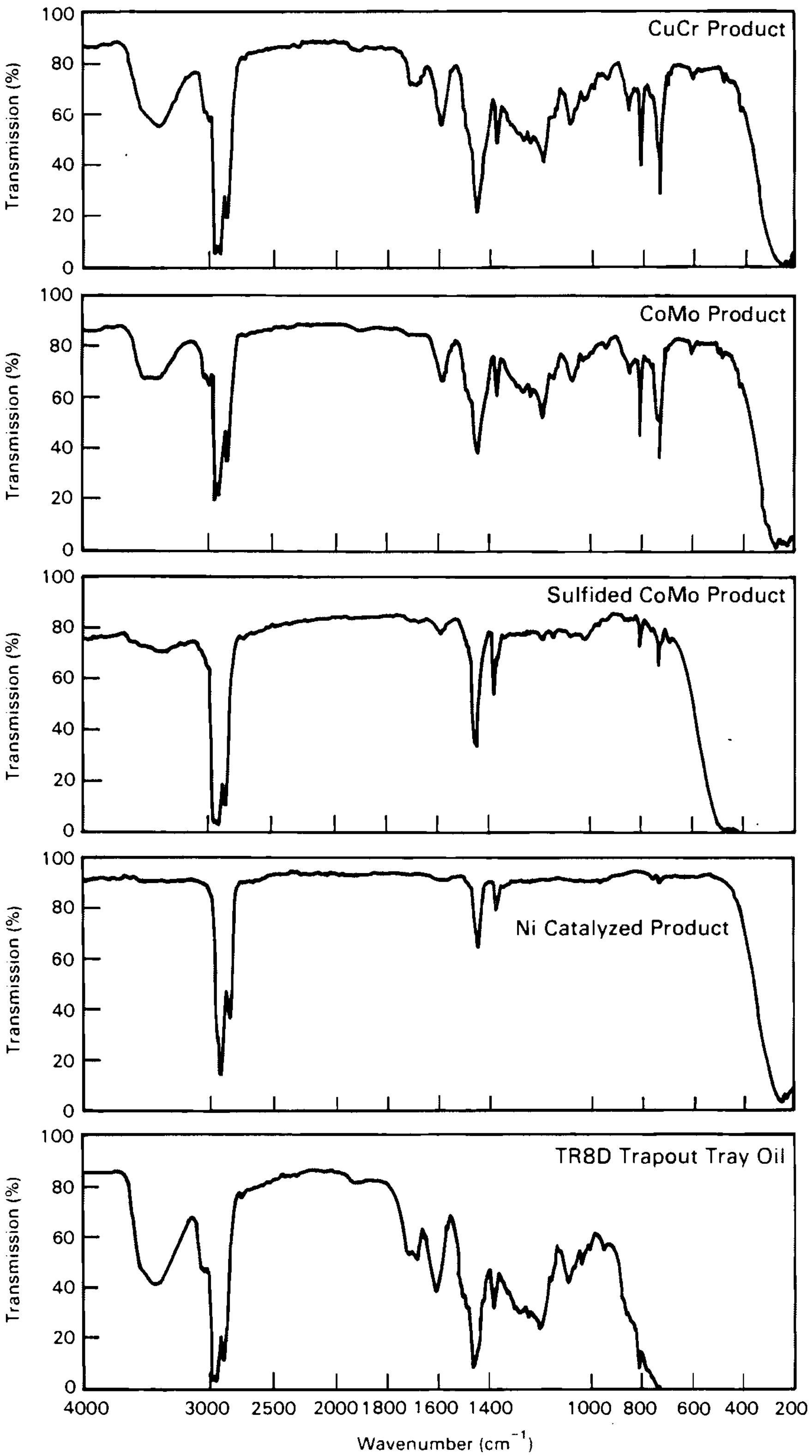

FIGURE 3. Infrared Spectra of Feedstock and Products from Hydrotreatment of Wood Liquefaction Distillate Oil

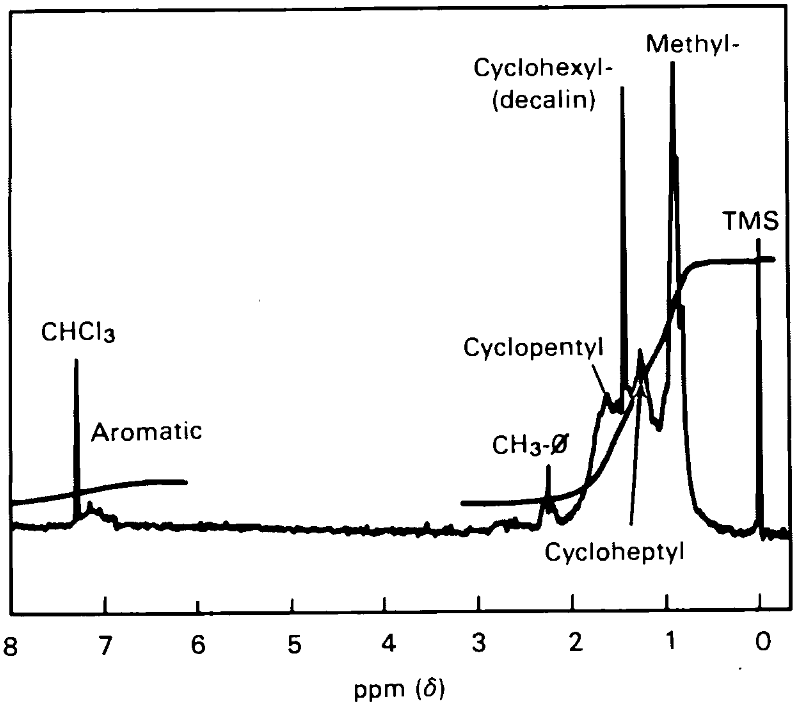

FIGURE 4. Proton Nuclear Magnetic Resonance Spectrum of Hydrotreated TR8D Trap-Out Tray Oil (nickel catalyst, 350°C, 2300 psig)

The nonsulfided cobalt-molybdenum (0402) catalyst showed only slight activity for either hydrogenation or deoxygenation. The results obtained with these four catalysts and the TR8D Trap-Out Tray Oil correlate very well with our earlier hydrotreating experience with these catalysts and phenol.

Carbon buildup on the catalyst pellets is significant in all cases. The sulfided cobalt-molybdenum (0402) exhibited slightly less carbon buildup (coke formation) than the unsulfided form and the nickel catalyst had the greatest amount of coke. The fact that methane production with the nickel catalyst occurred primarily early in the test and may have subsided as a result of the catalyst becoming coked should be investigated further. Like the methane formation, the coke formation percentage may merely be a phenomenon of the start-up of the nickel catalyst in this system. But this is only speculation, and for the present the data indicate that the combination of coke formation and methane formation with the nickel catalyst results in a significant reduction in liquid product yield.

Several important differences can be seen between the test with the TR7/12 distillate and the TR8D Trap-Out Tray Oil. As shown in Table 7, there is more coke formation on the catalyst with the TR7/12. One possible explanation for this difference may be the lower hydrogen-to-oil feed ratio. An

TABLE 8. Components of Hydrotreated Wood Liquefaction Distillate as Identified with Gas Chromatography/Mass Spectrometry

TR8D Trap-Out Tray Oil
Hydrotreated with Nickel Catalyst

Major	Minor
methylcyclohexane	trimethylcyclohexane
propylcyclohexane	methyldecahydronaphthalene
methylethylcyclohexane	hydrocarbon, 166 MW
dimethylcyclohexane	perhydroanthracene
C_3 cyclohexane	perhydrophenanthrene
C_2 cyclohexane	octahydrophenanthrene
(2)decahydronaphthalene	
methylpropylcyclohexane	
C_2 cyclohexane	
hydrocarbon, 126MW	

TR8D Trap-Out Tray Oil
Hydrotreated with Sulfided Cobalt-Molybdenum Catalyst

Major*	Minor*
methylcyclohexane	C_6 cycloalkane
cyclohexane	C_7 cycloalkane
C_2 cyclohexane	methylbenzene
trimethylbenzene	C_8 cycloalkane
C_3 benzene	trimethylcyclohexane
dimethylbenzene	(3) C_3 cyclohexanes
C_2 cyclohexane	dimethylbenzene
dihydroanthracene	propylcyclohexane
anthracene/phenanthrene	ethylmethylbenzene
acenaphthene/biphenyl	(5) C_4 benzenes
	methylisopropylbenzene
	(8) C_5 benzenes
	(2) C_7 benzenes
	methylisopropylphenol
	xanthene
	perhydroanthracene
	perhydrophenanthrene
	tetrahydrofluoranthene

* not strictly quantified, relative concentration as indicated by chromatograph peak area with flame ionization detector

C_x = x number of carbon atoms as alkyl substituents on the parent compound
(X) = number of isomers identified, if other than one
MW = molecular weight

alternate explanation for this difference may be the lower hydrogen partial pressure in the reactor due to the lower operating pressure and lower hydrogen-to-oil feed ratio. Still another possible explanation could be the difference in feed; TR7/12 distillate represents closer to 50% of the whole product as compared to only 35-40% for the TR8D Trap-Out Tray Oil. In addition, the TR8D Trap-Out Tray Oil contains a substantial contamination (10-25%) of anthracene oil, a coal-tar distillate used as the plant start-up slurry vehicle. Evidence of this contamination is found in the GC/MS data which include a number of multi-ringed aromatics and hydroaromatics, principally anthracene and phenanthrene and their hydrogenated counterparts. Possibly of greater importance is the fact that the TR7/12 distillate was in limited supply and, therefore, the experiment was comparatively short-lived. If the catalyst coking process is itself a short-lived process that reaches an equilibrium after a limited period of operation, then the relatively large proportion of carbon converted to coke in the TR7/12 experiment is merely a function of the short-term experiment, that is, the data do not represent steady-state operation relative to coke formation. This line of reasoning is supported by the similar levels of carbon found in the catalyst pellets following the two experiments (10.1-11.1% for TR8D Trap-Out Tray Oil and 12.0-12.1% for TR7/12 distillate).

The higher percentage of carbon converted to coke on the catalyst with the TR7/12 distillate may be a key to explaining the lower hydrogen consumption compared to the TR8D Trap-Out Tray Oil. Hydrogen gas formation coincidental with the coke formation may explain the apparently lesser consumption of hydrogen to transform the heavier, more oxygenated TR7-12 distillate to a more hydrogenated liquid product. The slightly longer residence time may have contributed to the slightly better product quality, but the liquid products themselves are quite similar for the two distillate feedstocks.

Biomass Liquefaction Product Whole Oil Hydrotreating

After the continuous-feed reactor had been shown to be functional and the catalyst activities could be verified with the distillate oil tests, the testing with the whole oils was begun in earnest. With the continuous-feed reactor more meaningful reaction kinetics could be obtained than in the batch reactor. Control of hydrogen partial pressure in the reactor was also facilitated by the gas flow system used in the continuous-feed reactor. The fixed bed of catalyst with the gas and oil feedstocks pumped through the bed also assured better mass transfer than in the spinning basket system used in the batch reactor. With the continuous-feed reactor, determinations could be made of the appropriate hydrotreating operating conditions and catalysts for the whole oils from direct liquefaction of biomass.

The catalyst choices for these experiments were based on our previous experiments with model compounds and distillate oils. Sulfided cobalt-molybdenum had been identified as having good hydrodeoxygenation activity while limiting hydrogen consumption through saturation of the aromatic systems. While the earlier tests had used a silica-alumina based cobalt-molybdenum (0402), the tests with whole oil were done with an alumina only supported cobalt-molybdenum (HT400) as described in Table 9. The HT400 catalyst is a "second generation" catalyst believed to be more active by the manufacturer. In addition, a nickel-molybdenum catalyst (HT500) was also tested instead of the nickel metal catalyst used earlier. The sulfided form of the nickel in combination with the molybdenum was expected to result in a less strongly hydrogenating catalyst which would produce less gas by-product and cause less saturation of the aromatic systems while maintaining a high activity for hydrodeoxygenation. As stated earlier, the specific catalysts used are those which were available through a commercial source and were tested as representatives of a type of catalyst. No determination has been made that these are the best individual catalysts for these purposes. The catalysts were used in their manufactured form and both were sulfided prior to the hydrotreating experiments.

TABLE 9. Catalysts Used in Hydrotreating Wood-Derived Whole Oils

Catalyst	Manfctr.'s Number	Manufacturer	Composition	Form
Cobalt-Molybdenum	HT400	Harshaw	3% CoO, 15% MoO_3 bal. Al_2O_3	1/8" extrudate
Nickel-Molybdenum	HT500	Harshaw	3.5% NiO, 15.5% MoO_3, bal. Al_2O_3	1/8" extrudate

Two whole oil feedstocks were tested in these experiments. Both products are from the Albany Biomass Liquefaction Experimental Facility. The first oil, designated TR7, was produced in an LBL-type process run (test run #TR7).

TABLE 10. Whole Oil Feedstock Analysis

	TR7 Oil		TR12 Oil	
	As Fed	Dry	As Fed	Dry
Carbon	73.9%	77.5%	72.6%	76.5%
Hydrogen	7.9%	7.9%	8.0%	7.8%
Oxygen	16.6%	14.1%	16.3%	12.5%
Nitrogen	<0.1%	<0.1%	<0.1%	<0.1%
Ash	0.5%	0.5%	3.0%	3.0%
Moisture	3.5%	0.0%	5.1%	0.0%
Density @ 55°C	1.10 g/ml		1.09 g/ml	
Carbon residue*	13.5%		26.9%	

---

*TGA simulated Conradson Carbon, see Reference 38.

The second, designated TR12, was produced in a PERC-type process run (test run #TR12). Details of the operating conditions during those tests are discussed elsewhere.(41) Detailed analysis of these products has also been reported(8) and is summarized in Table 10. The products are a black, tar-like material that is barely fluid at room temperature (pour point 23°C). Their chemical constituents are primarily phenolic and polyphenolic with some ketone functionality.

Procedure - The continuous-feed reactor system as described in the appendix was used for these tests. The Mode I/Mode II operations described in the appendix are important in these experiments. Mode I refers to operations in which the liquid feedstock is pumped at such rates that it is converted to light vapor products at the same rate that it is fed to the reactor such that no liquid overflow from the reactor occurs. The product from Mode I operations is nearly pure hydrocarbon which is condensed from the offgas product. Mode II operation refers to operations wherein the liquid feedstock is fed at faster rates than it is converted to light vapor products such that the product collected is a mixture of hydrocarbon products which were condensed after leaving the reactor as vapor and partially hydrotreated products which left the reactor in a liquid phase.

Results with TR7 Oil - Table 11 shows the results obtained by operation in Mode I with no liquid overflow for two catalysts at two temperatures, about 340°C and about 390°C. The oil feed rates in Table 11 represent the approximate maximum rate at which oil can be fed without allowing liquid overflow.

TABLE 11. TR7 Hydrotreating Data for Mode I Operation (no liquid overflow)

Experimental Parameters	16	17	11b	15a	15b	15c	14c
Catalyst	nickel-molybdenum		cobalt-molybdenum				
Temperature, °C	341	388	337	391	398	398	397
Pressure, psig	1995	2007	2011	2010	2003	2015	2019
Oil feed rate, ml/hr	34	47	71	96	81	108	68
Hydrogen rate, l/hr	132	144	120	180	168	84	174
LHSV, vol oil/vol cat/hr	0.04	0.05	0.08	0.11	0.09	0.12	0.08
Experimental Results							
Hydrogen consumption, l/l oil	947	938	730	660	616	407	670
Carbon conversion, wt% to gas (C_1 to C_4)	10.0	10.3	5.6	10.3	12.0	11.3	11.6
Product yield, ml/ml feed	1.10	1.10	1.14	0.96	0.99	0.93	1.01
Product analysis:							
Oxygen, %	0.7	0.6	0.7	0.0	0.0	0.3	0.03
Hydrogen to carbon ratio	1.97	1.97	1.79	1.51	1.65	1.40	1.61
Density, g/ml	0.803	0.798	0.807	0.885	0.836	0.926	0.832

With the cobalt-molybdenum (HT400) catalyst there was a significant difference in operations at 340°C and 390°C. Gas product yield increased from about 5% up to 12% (based on carbon) while hydrogen consumption (per liter of oil) remained essentially unchanged. A small increase in the maximum oil feed rate resulted at the higher temperature.

With the nickel-molybdenum catalyst there was little difference in gas yield or hydrogen consumption at 340°C and 390°C. The only noticeable difference was a 38% increase in the maximum feed rate that could be achieved.

Comparing the two catalysts, the cobalt-molybdenum (HT400) is about two times more active than the nickel-molybdenum catalyst as shown by the maximum oil feed rates that could be achieved. Hydrogen consumption is higher with the nickel-molybdenum catalyst and the liquid yield (ml product/ml oil fed) is about 10% higher. The relationship of these parameters to product quality will be discussed later.

The results obtained in Mode II operation with the cobalt-molybdenum (HT400) catalyst are shown in Table 12. Compared to Mode I operation, feed rates are much higher, hydrogen consumption is lower and product oil quality is much poorer.

Discussion of Results - In comparing the results with the two catalysts we see foremost the greater activity of the nickel-molybdenum toward attack of carbon-carbon bonds as shown by the greater saturation of oil (higher H/C ratio) and the large amount of hydrocarbon gas production even at the lower temperature. The amount of oxygen remaining in the nickel-molybdenum products is low, yet may actually be higher than that in the cobalt-molybdenum (HT400) products. The lower rate of production of gasoline-range hydrocarbons with the nickel-molybdenum catalyst implies that its catalysis of the combined hydrogenation reactions is not as effective as that of the cobalt-molybdenum (HT400).

The effect of temperature on the product composition is significant only in the case of the cobalt-molybdenum (HT400) catalyst. The higher temperature operation (390-400°C) results in a markedly reduced level of saturation of the liquid product at the same time that greater amounts of gaseous hydrocarbons are being formed. Whereas the high quality product at about 350°C has a H/C ratio near 1.8, the product at elevated temperature drops to 1.65 or below. In those high temperature products with H/C ratios below about 1.6, there was a dramatic increase in density as well as a significant reduction in gasoline range hydrocarbon (as shown by distillation of the products). It is possible

TABLE 12. TR7 Hydrotreating Data for Mode II Operation (liquid overflow)

Experimental Parameters	12a	13a	14a	14b
Catalyst	cobalt-molybdenum (HT400)			
Temperature, °C	330	335	389	394
Pressure, psig	2017	2008	2026	2021
Oil feed rate, ml/hr	296	302	498	270
Hydrogen rate, l/hr	120	197	180	170
LHSV, vol oil/vol cat/hr	0.33	0.33	0.55	0.30
Experimental Results				
Hydrogen consumption, l/l oil	277	278	202	435
Carbon conversion, wt% to gas (C_1 to C_4)	1.1	2.4	1.8	5.5
Product yield, ml/ml feed	0.98	0.99	0.88	1.01
Product analysis:				
Oxygen, %	3.6	4.8	2.6	1.1
Hydrogen to carbon ratio	1.35	1.33	1.32	1.41
Density, g/ml	0.96	0.971	0.956	0.913

that the difference in these products may result from the volatilization from the reactor of higher molecular weight or more aromatic components due to their increased vapor pressure at higher operating temperature. By this mechanism the higher molecular weight or more aromatic components could leave the reactor prior to their hydrogenation. Analysis by carbon-13 nuclear magnetic resonance spectrometry provides additional information on the differences in product quality. Results to date have shown that the difference between the 14c (397°C) product and the 11b (337°C) product lies primarily in the amount of aromatic character. The 14c product has a ratio of 36 to 64 percent aromatic to aliphatic carbon while the 11b product ratio is 22 to 78. The amount of substitution in either case is nearly the same with two carbons per aromatic ring carrying an aliphatic side chain of at least one carbon. These two products are both essentially all gasoline range hydrocarbon.

The effect of gas and liquid flow seems to also have a significant impact on the extent of hydrogenation which occurs. Products 15a and 15c both appear to be volatilized hydrocarbon products yet both have greatly reduced H/C ratios. The 15a product results from a higher oil feed rate while the 15c product results from a decreased gas feed rate. In both cases the reduced partial pressure of hydrogen within the reactor has apparently resulted in the formation of highly aromatic products. The 15c product contains such a large fraction of aromatics (from dimethylindans to phenylenepyrene) that it contains only 36% gasoline fraction by distillation and its viscosity is noticeably increased (4.6 centipoise at 37°C). Both the 15a and c products have higher densities and lower heats of combustion as the result of being less saturated but not due to higher oxygen contents.

Additional analyses, other than elemental composition and density, have been used on several of the products to further define their properties. The viscosities of these products have been measured at 1.0 to 1.2 centipoise at 35°C. The heats of combustion have been in the range of 10510 to 10830 cal/g (18900-19500 Btu/lb). As mentioned earlier the amount of aromatic carbon as measured by carbon-13 NMR has ranged up to 36 percent in these same products with approximately 1/3 of the aromatic sites substituted with an aliphatic side chain. This information can be used to calculate an alkylated hydrocarbon ratio of 1.1 to 1 naphthenic to aromatic. In other words, about half of the product retains the aromatic character of the feedstock while the other half is saturated but retains the cyclic character of the feedstock.

Inspection of the infrared spectra for these products provides additional evidence of the chemical reactions involved. Figure 5 includes spectra of the TR7 feedstock and the products with the nickel and the cobalt-molybdenum (HT400) catalysts. First, it should be stated that by comparison of these product spectra with the distillate oil spectrum in Figure 5, it is clear that these products are not merely distillates but have actually undergone chemical changes. The nickel-catalyzed product in Figure 5 shows reduced aromatic (3010, 1590, 1500 cm^{-1}), carbonyl (1720, 1690 cm^{-1}), and hydroxyl bands (3300-3400 cm^{-1}) compared to the TR7 product. In the case of the cobalt-molybdenum (HT400) catalyst, the Mode I product is essentially devoid of carbonyl and hydroxyl character. The product is highly aliphatic (2950, 2920, 2850, 1450, and 1370 cm^{-1}) with strong evidence of aromatic character. In comparison with the product from the distillate oil, this product from TR7 whole product oil actually

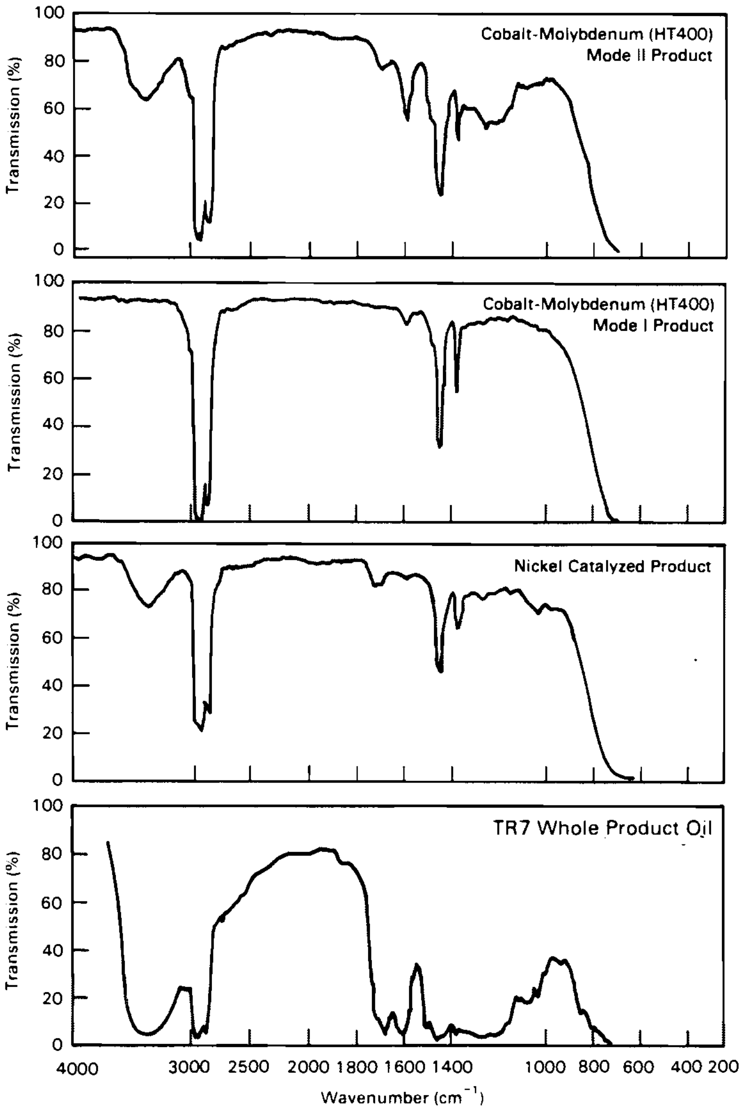

FIGURE 5. Infrared Spectra of Feedstock and Products from Hydrotreatment of Wood Liquefaction Product at 350°C

exhibits less hydroxyl and carbonyl absorption with more aromatic character. The Mode II product from the cobalt-molybdenum (HT400) test appears to be similar to the nickel-catalyzed products except for stronger aromatic absorption bands.

The use of capillary gas chromatography provides an interesting comparison of the hydrotreated product and the feedstock. Figure 6 shows a chromatograph for the TR7 whole oil feedstock while Figure 7 shows a chromatograph for the Mode I product from the cobalt-molybdenum (HT400) test produced at similar conditions. The peak identifications were provided by related GC/MS analysis. The difference in component identity as well as volatility is obvious. The TR7 product is a collection of cyclic ketones and phenolics and the hydrotreated product contains a combination of aliphatic and aromatic hydrocarbons.

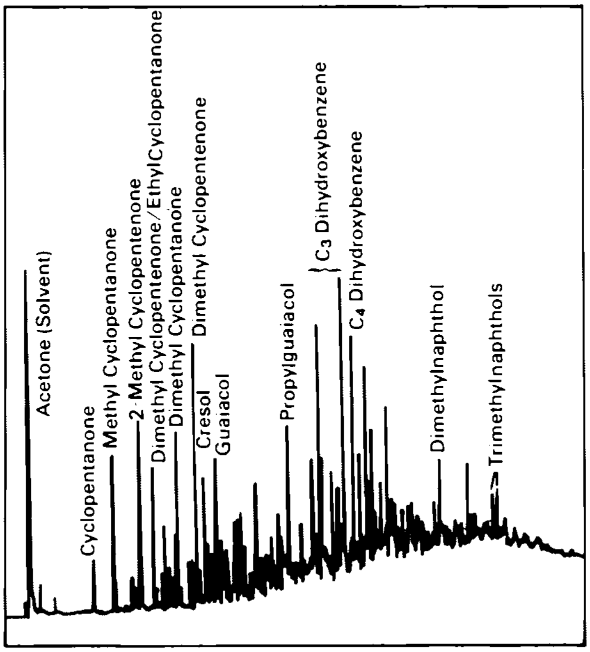

FIGURE 6. Capillary Gas Chromatography of Wood Liquefaction Product

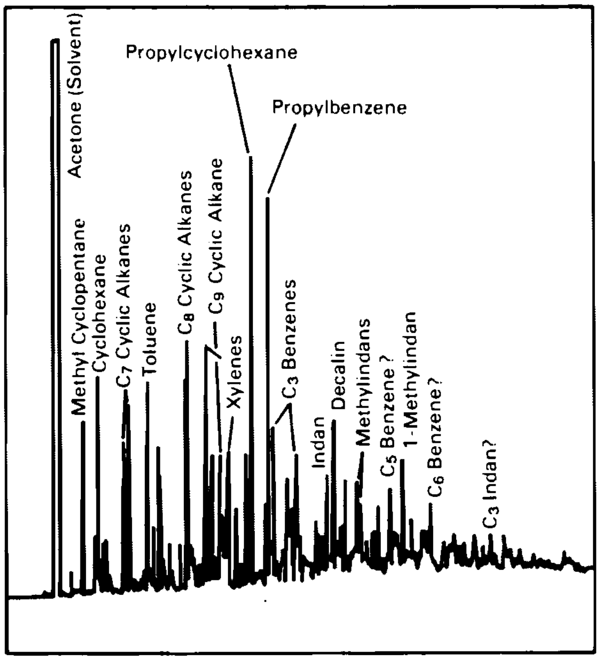

FIGURE 7. Capillary Gas Chromatography of Hydrotreated Wood Liquefaction Product (cobalt-molybdenum (HT400), 345°C, 2400 psig)

Distillation can be used as a measure of processing effect on the quality of product produced. Figure 8 presents the distillation curves for these products. The maximum distillation temperature limits as set by the American Society for Testing and Materials (ASTM) are superimposed on the distillation curves. The comparison to the ASTM limits shows that the Mode I product from the cobalt-molybdenum (HT400) test nearly falls within the distillation range for gasoline. The nickel catalyzed product is not nearly so close to the gasoline limits being somewhat heavier than the cobalt-molybdenum (HT400) product. Most interesting of all is the sharp contrast of the Mode I and Mode II products from the cobalt-molybdenum (HT400) test. Although the elemental oxygen content was similar between the nickel product and the Mode II cobalt-molybdenum (HT400) product, the distillation curves show that these products are drastically different with respect to volatility. In fact, the distillation curve from the Mode II cobalt-molybdenum (HT400) product appears to be a summation of the distillation curve from the Mode I hydrotreated product and

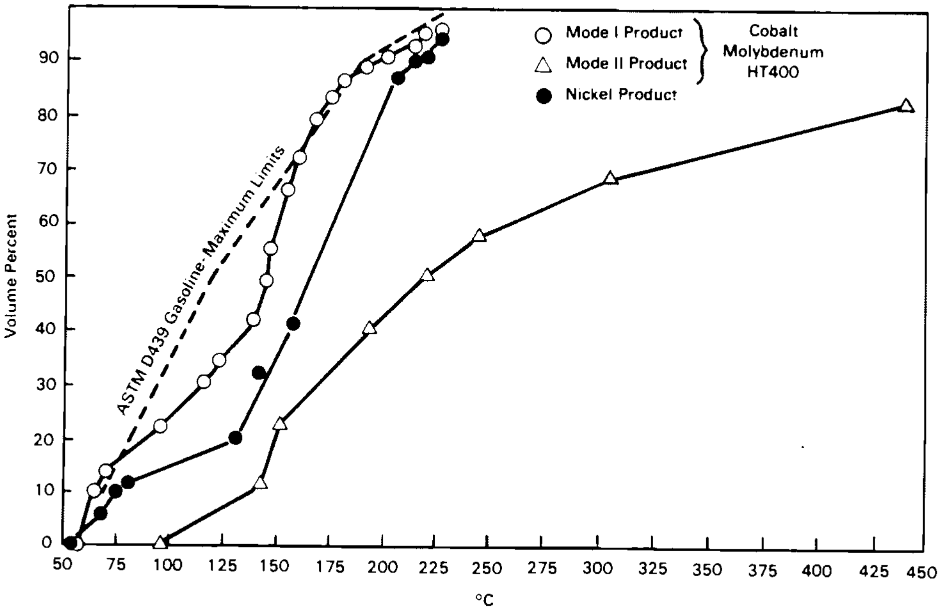

FIGURE 8. Atmospheric Distillation Curves for Hydrotreated Wood Liquefaction Products

the distillation curve of TR7 product.(7) The Mode II cobalt-molybdenum (HT400) product is only slightly lighter than the residual material recovered from the reactor following termination of the test.

The use of a sulfided catalyst with a low-sulfur feedstock has been a concern since the early stages of this work with model compounds. We have noted that some amount of the sulfur has been coming out with the products. The amount has now been quantified and found to be very low. Although initial products have contained up to 350 ppm of sulfur, after several hours of operation the sulfur content in the product has dropped to 47-63 ppm, similar to the feedstock itself (<45 ppm). One attempt was made to resulfide the catalyst between experiments by the addition of H_2S to the reactor with heating. Although the sulfiding step has been found to be a highly exothermic reaction with fresh catalyst, a much lesser amount of exothermicity was noted during the resulfiding procedure. Following resulfiding no significant difference in catalyst activity was noted; however, product sulfur content jumped back up to

293 ppm before decreasing again in a later sample. The amount of sulfur in the active catalyst has not been measured and the effect of sulfur losses over long periods of operation has not been determined. Use of the sulfided cobalt-molybdenum (HT400) for up to ten hours was demonstrated by these experiments. These tests included heat-up and cool-down cycles without measurable loss of catalyst activity.

Results with TR12 Oil - Four tests were also completed with the TR12 (Albany PERC-type) oil; actually, there were two sets of tests with two tests at about 350°C and two more at about 400°C. The sulfided cobalt-molybdenum catalyst (HT400) was used in all four tests. The product analysis data, given at the bottom of Table 13 demonstrate that the same high quality hydrocarbon liquid product can be produced from Mode I operation with the TR12 at similar conditions as used earlier in Mode I operations with the TR7 oil (see Table 11). A similar gasoline-like product is produced which is low in oxygen with a H/C ratio indicative of a mix of aromatic and cyclic hydrocarbons. However, the gas production is higher with the TR12 and, as a result, the hydrogen consumption is also higher. The gas product is primarily methane with only traces of higher hydrocarbon.

Discussion of Results with TR12 Oil - A significant difference between the TR12 and TR7 tests is the imbalance which developed between the carbon input and output. While the oxygen input and output was fairly balanced, a holdup of carbon within the reactor was evident at presumed steady-state operating conditions. This imbalance suggests that the hydrodeoxygenation proceeds quickly while the hydrocracking to reduce molecular weight proceeds more slowly. In this manner, the oxygen is removed from the wood-oil as water and is readily flashed out of the reactor while the remaining hydrocarbon (mostly deoxygenated) is of such a structure that it remains nonvolatile until additional reaction can occur. The nonvolatile carbon could be remaining in the reactor in any one of at least three forms which have been identified:

- a heavy oil (intermediate between the feedstock and the light product) which is recovered from the reactor at the end of each test and should conceivably be converted to light product by extended residence time in the reactor and additional consumption of hydrogen gas

TABLE 13. TR12 Oil Hydrotreating Data

Experimental Parameters	↓[a] 18a	18b	19	↓[a] 20a	20b	21
Catalyst	cobalt-molybdenum (HT400)					
Temperature, °C	346	341	336	432	436	407
Pressure, PSIG	1990	1995	2002	2005	2005	1995
Oil Feed Rate, ml/hr						
(actual)	98	117	37.3	357	268	125
(based on carbon[b])	44.4	60.2		181	122	46
Hydrogen Rate, l/hr	180	306	168	162	168	204
Experimental Results						
Hydrogen Consumption l/l oil[b]	853	836	1093	714	697	665
Carbon Conversion, wt% to gas	13	15	25	23	14	13
Product Yield, ml/ml feed	1.02	1.0	0.84	0.88	0.91	0.97
Carbon Balance (actual)	45	51	94	51	46	37
Hydrogen Balance (actual)	90	82	103	81	98	
Oxygen Balance (actual)	273	186	200	197	220	301
(based on carbon[b])	123	96		100	100	113
Product Analysis:						
Oxygen %	0.5	0.4	0.6	0.8	0.9	0.0
H/C ratio	1.93	1.90	1.72	1.68	1.68	1.64

---

a = new catalyst charged to reactor
b = flows and balances calculated to achieve 100% balance of carbon input and output

- a coke-like solid which is insoluble in acetone and does not melt which is unlikely to be converted to light product, and
- carbon-containing deposits on the catalyst pellets which have been determined to have reached a steady-state concentration on the catalyst after several hours of operation.

Further evaluation of the test results with the TR7 fed through the nickel-molybdenum catalyst also show that carbon imbalance was a significant factor in those tests. The imbalance can be attributed to the same three forms of carbon found in the reactor following the experiments. The short-term nature of the tests seems to be a partial explanation for an even greater carbon imbalance found in the nickel-molybdenum catalyst tests. Yet the more obvious reason for the difference in conversion to light products would be a different catalytic mechanism. Detailed chemical analysis of the partially hydrotreated oil recovered from the reactor after the test should provide important clues to the reason for the difference in effective conversion between the two catalysts and between the two oil feedstocks.

Carbon deposition on the catalyst has also been considered as a potential means of catalyst deactivation. Carbon deposition has been determined to occur during the start-up of the reactor as catalyst is first exposed to the feedstock resulting in strongly exothermic reactions. The carbon deposition reaches an apparent steady state within about the first hour of operation and appears to remain nearly constant thereafter. These conclusions were suggested by our earlier tests wherein carbon deposition was measured at 7.3 to 12.8 percent on sulfided cobalt-molybdenum (0402) catalyst after 3.5-4.0 hours of operation with the TR7 feed. An earlier test with a TR7 distillate feedstock at the same conditions and catalyst resulted in 12.0-12.1% carbon deposition after only one hour.

Further testing of the reactor residues has now shown that there is a significant difference in the coke formation on the cobalt-molybdenum (HT400) and nickel-molybdenum catalysts used with the TR7 feedstock. As shown in Table 14 the amount of carbon deposited on the catalyst pellets which cannot be rinsed off with acetone is only half as great on the cobalt-molybdenum (HT400) catalyst. The range of carbon numbers found in Table 14 fairly covers the range reported in the literature of carbon laydown on active hydrotreating catalysts. The variation in the carbon reported in Table 14 for a given catalyst and temperature relates the variation within the reactor bed. The results of three analyses (top, middle, and bottom of the catalyst bed) are generally reported in Table 14. The data from Table 14 also suggests that there is little difference in the carbon deposition between the TR12 and TR7 feedstocks.

TABLE 14. Carbon Deposition on Hydrotreating Catalysts

	TR7, 350°C	TR7, 400°C	TR12, 350°C
cobalt-molybdenum (HT400)			
top of bed	---	6.7	5.6
middle of bed	9.0	8.2	6.6
bottom of bed	---	---	11.6
nickel-molybdenum			
top of bed	4.0	6.2	no experiment performed
middle of bed	17.8	22.2	
bottom of bed	18.2	---	

Weight percent of carbon in ground catalyst pellets recovered after the experiment

Other carbon deposition as coke-like material in the catalyst bed has also been noted. This material tends to form in the quiescent portions of the bed and produces a loosely bound catalyst/char conglomerate which breaks up during removal of the catalyst bed. It is difficult to directly determine the amount and composition of this carbon-rich residue but calculations-by-difference based on the catalyst charged suggest that up to 10% of the oil fed may be included in this conglomerate. Only longer-term experimentation (continuous operation of 20 to 40 hours) can actually provide answers as to the amount of buildup of unconvertible material within the hydrotreater as well as the long-term stability of the catalyst.

HYDROTREATING PYROLYZATE OILS

A number of attempts have been made in recent years to upgrade biomass pyrolyzates to hydrocarbon fuels. The results have been somewhat mixed as described in the Background section of this report. Our own results of catalytic hydrotreating pyrolyzates were also, initially, unsuccessful. Our use of the sulfided cobalt-molybdenum catalyst at 350°C and 2000 psig produced only limited quantities of hydrocarbon product before the catalytic bed plugged with a coke-like material. Based on these results we realigned our experimentation to test alternate processing conditions, but first we studied the thermal instability of the pyrolysis oils.

When performing thermochemical upgrading on these pyrolysis oils, their thermal instability is a major consideration. This instability is suggested by coking of the oil during batch distillations and decomposition of the oil at elevated temperatures under inert atmosphere. We have reported previously a number of instances of coke formation during distillation of pyrolyzates (17,42,43,44). The batch distillation of these oils under vacuum (10-25 mm Hg) proceeds routinely until a pot temperature of 170-200°C is attained at which point a strongly exothermic reaction occurs and the bubbling oil solidifies into a sponge-like coke. This phenomenon is totally unlike the distillation of the high-pressure oils which proceeds to temperatures of 300°C or greater without coking of the distillation residue.

In another type of test we have reported that pyrolyzates will decompose to a solid and a water solution when heated to 270°C when sealed under inert gas.(43) This effect was found for several whole pyrolyzates as well as an oil distillate, a light-distillate-stripped oil, a water-washed oil, an aqueous sodium carbonate-extracted (acid-free) oil. All these results compare with our earlier report of a lack of change in high-pressure liquefaction products under the same conditions of thermal stress. Apparently, the thermal instability of pyrolyzates cannot be attributed solely to either the low- or high-molecular weight components nor can it be altered by removal of the acid fraction nor by the separation of water soluble components.

Given this lower level of thermal stability for the pyrolyzates as compared to high-pressure oils, processing methods must be designed either to overcome the instability or incorporate it into the processing mechanism. Based on our early results with catalytic hydrotreating, we concluded that we could not overcome the thermal decomposition by a conventional catalytic hydrogenation. We therefore modified our approach to incorporate the decomposition into the process. Whereas, the apparent rate of thermal decomposition to coke is much greater than that of catalytic hydrodeoxygenation at temperatures of approximately 350°C; we attempted to process the pyrolyzate at a lower temperature where the rate of thermal decomposition would be slower and, potentially, more in balance with the rate of catalytic hydrodeoxygenation. In addition, the more active hydrogenation catalyst nickel was used in an attempt to further offset the effect of the thermal decomposition reactions. However, our tests soon demonstrated that the sulfided cobalt-molybdenum catalyst was also as effective as the nickel at hydrotreating at the lower temperatures.

Procedure

The reaction system used for these tests was the continuous-feed fixed-bed catalytic system described in the appendix. The catalysts tested included the cobalt-molybdenum catalyst (HT400) used in the high-pressure oil upgrading tests and a high concentration nickel on alumina catalyst. The nickel (3266) catalyst was chosen for its open pore structure which should be more accessible to the large pyrolysis oil components. The catalysts are described in Table 15. As stated earlier, the specific catalysts used are those which were available through a commercial source and were tested as representatives of a type of catalyst. No determination has been made that these are the best individual catalysts for these purposes. The catalysts were used in their manufactured form except that the cobalt-molybdenum was sulfided and the nickel was reduced prior to the hydrotreating experiments.

TABLE 15. Catalysts Used in Hydrotreating Pyrolysis Oils

Catalyst	Manfctr's Number	Manufacturer	Composition	Form
Nickel	Ni3266	Harshaw	50% Ni on silica/ alumina	1/16" extrudate
Cobalt-Molybdenum	HT400	Harshaw	3% CoO, 15% MoO_3 bal. Al_2O_3	1/8" extrudate

The pyrolysis oil used in these experiments was produced in the Georgia Tech entrained flow pyrolysis reactor.(16). Typical analysis of the feedstock is given in Table 16. The Georgia Tech pyrolyzates are believed to be

TABLE 16. Pyrolysis Oil Analysis

	As Fed	Dry
Carbon	39.5%	55.8%
Hydrogen	7.5%	6.1%
Oxygen	52.6%	37.9%
Nitrogen	$<$0.1%	$<$0.1%
Ash	0.2%	0.3%
Moisture	29.0%	0%
density	1.23 g/ml @ 55°C	--

representative of the flash pyrolysis products being studied in several laboratories. They are a hardwood derived product and as such contain a significant proportion of dimethoxyl phenolics as remnants of the hardwood lignin. The Georgia Tech products are not atypical of hardwood products in this respect but this composition does differentiate the Georgia Tech products from flash pyrolyzates produced from softwoods.

Results and Discussion

Since our initial experience with pyrolyzate oil indicated that operating temperature was an important consideration, the first experiments planned were to determine the effect of temperature on the catalytic system. Following the initial determination of allowable operating temperature, catalyst content, space velocity (residence time) and hydrogen partial pressure were varied to determine their effects.

Effect of Temperature - The initial attempt to hydrotreat pyrolyzate at PNL was made with a flash pyrolysis oil from the University of Waterloo(17) at 350°C over a sulfided cobalt-molybdenum catalyst. As mentioned above, this test was terminated prematurely when the catalyst bed plugged. With this knowledge in hand, a series of tests with pyrolyzate from the Georgia Tech entrained-flow pyrolysis unit were initiated. These tests were to examine the operating temperature range of 250 to 350°C in the presence of a nickel catalyst which was expected to be a more active hydrogenation catalyst. Given the lower temperatures to lessen thermal decomposition and a more active catalyst it was intended to achieve a balance between decomposition and hydrogenation.

The low temperature operating conditions proved effective in allowing stable operations in the reaction system. However, the product of this type of processing is far from the gasoline-like material produced from the high-pressure oil at higher temperature. Table 17 provides a list of important operating conditions for a series of tests over the temperature range from 250°C to 310°C. Operation of the system at temperatures much above 300°C led to excessive thermal decomposition and plugging in the catalytic bed.

The processing results from these tests show that this temperature range is the critical range in the balance of catalytic hydrogenation and thermal decomposition of the pyrolyzates. The low temperature test at 258°C proceeded smoothly. It produced a relatively uniform product oil and resulted in only minor amounts of char formation in the catalyst bed. The carbon loading on the catalyst varied from 5.5 to 10 percent at the end of the test. The bulk of the carbon missing in the carbon balance is suspected to have been product oil which was unknowingly washed from the product letdown train during system cleanup following the test.

The middle temperature test at 280°C also proceeded smoothly, however, a lighter more deoxygenated product was recovered earlier in the run before the heavier components reached the knock-out pot. This product variation represents the more hydrotreated components which were produced at higher temperature and which traveled out of the reaction vessel more readily due to their greater volatility and the higher temperature of operation. A pressure drop across the reaction vessel developed during the run which indicated a partial blockage of the system. However, the pressure drop dissipated later in the run and the experiment was terminated voluntarily. A much larger amount of char material was found in the partially hydrotreated oil left in the reaction vessel following this test. The catalyst pellets carried a higher carbon loading (7-13%) although the total amount of carbon as a percent of feed carbon was about the same as in the 258°C test.

In the high temperature test at 310°C the reaction vessel eventually plugged and the experiment had to be terminated. The product oil recovered during this test was of a better quality than even the lighter products from the 280°C test. At the end of this test the catalyst bed was completely encased in a brittle, high melting polymer material. The interpretation of this result is that the thermal decomposition leading to coking of the pyrolyzate proceeds at a greater rate than the catalytic hydrogenation process at 310°C. Carbon conversion to gas at 310°C was the highest in any of the three tests.

TABLE 17. Hydrotreating Test Results with Georgia Tech Pyrolyzate

Experimental Operating Conditions			
Catalyst	nickel	nickel	nickel
Temperature, ^{o}C	258	280	310
Pressure, PSIG	2020	2050	2050
Oil feed rate, ml/hr	290	396	405
Hydrogen rate, l/hr	168	216	240
LHSV, vol oil/vol cat/hr	0.32	0.44	0.45
Hydrogen consumption, l/l oil	66	161	252

Experimental Results and Product Analyses			
Carbon conversion, wt%			
to oil/aqueous	36/14	57/10	0/5
to gas (C_1 to C_4	9	11	16
to carbon on catalyst	9	8	--
Oil product yield, ml/ml feed	0.28	0.42	reactor plugged
Carbon balance (based on oil/aqueous/gas	59	78	--
Hydrogen balance	91	100	--
Oxygen balance	100	102	--
Overall mass balance	84	96	--
Total oil feed, ml	1601	1737	2026
Wet product analysis			
H/C, atomic	1.54	1.42	1.49/1.63
oxygen, percent	26.8	25.0	19.4/13.2
density, g/ml	1.1	--	-- /0.96

Effect of Catalyst - The result with the nickel catalyst at 310°C (plugged reaction vessel) was similar to that achieved at higher temperature with the cobalt-molybdenum catalyst. In order to provide a more direct comparison of the two catalysts, tests were undertaken with the sulfided cobalt-molybdenum catalyst at lower temperatures. As shown in Table 18, in nearly all respects the nickel catalyzed tests provided the same results as the cobalt-molybdenum catalyzed tests.

A single test with alumina balls in place of alumina-supported metal demonstrated that the catalytic entity is important to the process. With only alumina in the bed (results in Table 18) the reaction vessel plugged almost immediately. Only limited amounts of water and heavy oil product (24-28% oxygen) were recovered prior to the system plugging. A coke-like material (Hydrogen to carbon atomic ratio 1.04) was recovered from the bottom one-third of the reactor. We conclude that although the net hydrogen consumption in the metal catalyzed tests was relatively small, the metal catalyst must play a key role in interrupting the thermal decomposition/polymerization of the pyrolyzate, probably by hydrogenating active intermediates.

Effect of Residence Time - Since the thermal decomposition reactions are perceived to be relatively fast reactions and since little catalytic hydrogenation appears to be occurring in the reaction vessel (as measured by hydrogen consumption) it was recognized that the length of time in the reaction vessel might play a relatively minor role in this processing. Indeed, as the data in Table 19 shows, there is almost no effect on the product quality as a function of residence time. As the residence time is reduced from 86 minutes to 23 minutes the oxygen content and hydrogen to carbon ratio of the products remains almost unchanged. Additional reduction in residence time was limited by the experimental equipment so that the minimum required processing time has not yet been determined. The differences in the product quality numbers in Table 5 are explained by minor differences (± 2%) of water dissolved or emulsified in the product oils. The initial abrupt change in oxygen content of the product tar in going from 86 to 66 minutes is thought to be related to the hydrogen partial pressure change (see next section). Changes which are noticeable as a function of residence time are the decrease in gas production and increase in oil product recovery as the residence time decreases. Coincidentally, the amount of oxygen rejection from the oil phase also decreases. These results suggest that the low temperature hydrotreating to upgrade pyrolyzates can be accomplished with relatively fast throughputs and residence times of 23 minutes or less.

TABLE 18. Additional Hydrotreating Test Results

Experimental Operating Conditions		
Catalyst	CoMo	Alumina
Temperature, °C	273	254
Pressure, psig	2025	2000
Oil feed rate, ml/hr	392	411
Hydrogen rate, l/hr	168	180
LHSV, vol oil/vol cat/hr	0.44	0.46
Experimental Results and Product Analyses		
Hydrogen consumption, l/l oil	135	-49
Carbon Conversion, wt %		
to oil/aqueous	55/11	--
to gas (C_1 to C_4)	9	10
Oil product yield, ml/ml feed	0.42	reactor plugged
Carbon balance (based on oil/aqueous/gas)	70	--
Hydrogen balance	96	--
Oxygen balance	104	--
Overall mass balance	91	--
Total oil feed, ml	1794	753
Wet Product Analysis		
H/C atomic	1.47	1.14
oxygen, percent	24.6	24.9

TABLE 19. Pyrolyzate Hydrotreating Results as a Function of Residence Time

Experimental Operating Conditions

Catalyst	CoMo	CoMo	CoMo	CoMo	CoMo	CoMo
Temperature, °C	273	271	271	274	271	270
Pressure, psig	2025	2020	2020	2010	2030	2040
Oil feed rate, ml/hr	392	515	555	935	1200	1440
Hydrogen rate, l/hr	168	120	120	120	120	120
LHSV, vol oil/vol cat/hr	0.44	0.57	0.62	1.04	1.33	1.60
Residence Time, min	86	66	61	37	28	23

Experimental Results and Product Analyses

Hydrogen consumption, l/l oil	135	90	60	39	32	28
Carbon Conversion, wt %						
to oil/aqueous	82/11	80/10	87/8	83/5	83/7	87/11
to gas (C_1 to C_4)	9	7	7	5	4	4
Oil product yield, ml/ml feed	0.52	0.56	0.69	0.66	0.65	0.70
Carbon balance	100	97	102	93	94	102
Hydrogen balance	103	104	97	81	81	96
Oxygen balance	100	99	100	76	77	97
Overall mass balance	100	98	101	83	84	99
Total oil feed, ml	1794	3860	3890	2683	1872	2123
<u>Wet Product Analysis</u>						
H/C atomic	1.47	1.47	1.56	1.56	1.48	1.58
oxygen, percent	24.6	30.8	32.7	32.7	31.4	34.2
Oxygen rejection, %	79	70	57	59	62	55

Effect of Hydrogen - A series of experimental conditions were tested in order to evaluate the need for adding hydrogen to the reaction vessel. This series of experiments was performed at the highest oil flow rate tested in the previous section. In the series, the hydrogen flow was reduced in steps to zero then the pressure maintained in the reaction vessel was reduced in steps to only 200 psig. Operations continued successfully throughout the series of conditions without coking and plugging of the reaction vessel until the experiment was terminated and oil flow was stopped. At that point a combination of the thermal inertia in the heaters and exothermic reactions in the vessel led to a temperature increase of over 50°C and the oil in the vessel coked to a solid. The coking precluded any restart attempt and emphasized the delicate balance of temperature, residence time, and hydrogen partial pressure which must be maintained during the low temperature catalytic treatment of the pyrolyzates.

In addition to the product quality data given in Table 20 there were other indicators of a general product quality loss as the amount of hydrogen in the system was reduced. The viscosity of the product increased from 14,200 centipoise @ 60°C for the products at the higher hydrogen flows to 18,700 centipoise @ 60°C for product with low hydrogen flow to 32,700 centipoise @ 60°C for the product with no hydrogen flow. These viscosities range upward from those measured for the high-pressure oils and are about three orders of magnitude higher than the viscosity measured for the crude pyrolysis oil. An increase in density was also found to correlate with the reduction in hydrogen flow. Densities increased from 1.14 to 1.16 to 1.18 g/ml @ 20°C for the products of higher flow, lower flow and no flow of hydrogen, respectively. These densities again range upward from that measured for a high-pressure oil while remaining less than the typical density of a pyrolysis oil.

Product Analysis of Low-Temperature Treated Pyrolyzate - The results given above indicate that the low-temperature catalytic treatment of pyrolyzate transforms the primary pyrolyzate oils into a chemical composition similar to that of the high-pressure oils. Further analysis has confirmed this conclusion. The 258°C product has been distilled to recover 2% light hydrocarbon, 29% distillate and 59% residual material with 9.5% water dissolved in the oil. The distillation was taken to an endpoint of 205°C @ 20 mmHg. The presence of small water droplets in the condensate at temperatures approaching the end point indicated that thermal cracking of the oil

TABLE 20. Hydrotreating Results as a Function of Hydrogen Flow

Experimental Operating Conditions				
Catalyst	CoMo	CoMo	CoMo	CoMo
Temperature, ^{o}C	270	277	276	268
Pressure, psig	2040	2028	2010	200
Oil feed rate, ml/hr	1440	934	959	1062
Hydrogen rate, l/hr	120	40	0	0
LHSV, vol oil/vol cat/hr	1.60	1.04	1.07	1.18
Residence time, min	23	37	37	33
Experimental Results and Product Analyses				
Hydrogen consumption, l/l oil	28	26	0	0
Carbon Conversion, wt %				
to oil/aqueous	87/11	83/9	85/7	85/10
to gas (C_1 to C_4)	4	10	10	5
Oil product yield, ml/ml feed	0.70	0.61	0.61	0.68
Carbon balance	102	102	103	100
Hydrogen balance	96	92	92	101
Oxygen balance	97	97	94	99
Overall mass balance	99	99	98	100
Total oil feed, ml	2123	1900	1618	1300
Wet Product Analysis				
H/C atomic	1.58	1.44	1.33	1.62
oxygen, percent	34.2	30.7	29.5	35.8
Oxygen rejection, %	55	61	62	48

was occurring and the distillation was terminated. The residual material was still fluid and had not coked at a pot temperature of 280°C. This behavior contrasts sharply with the thermal decomposition and coke formation at $<200^{\circ}$C experienced with the pyrolyzate feedstock and is more similar to the behavior of the high-pressure oils.

The thermal stability of the low-temperature, hydrotreated product oil as well as its elemental composition (70.7%C, 8.1%H, 0.1%N, 20.9%O, calculated to a dry basis) indicate that it has been significantly upgraded from the original pyrolyzate. Chemical composition analysis by GC/MS was performed on one sample and the identified components are listed in Table 21. The carbonyl side chains which could be a major source of polymerization of the phenolics have been destroyed. Unsaturated alkyl side chains (propenyl) have been saturated. The relative amount of phenolic material appears to have increased at the expense of the phenolic ethers. Saturated cyclic alcohols (cyclohexanols) are also present indicating some hydrogenation of the aromatic rings. Also detected were pure hydrocarbon compounds such as the tetralins (tetrahydronaphthalenes). The acid component is largely removed into the aqueous phase and should no longer interfere in the hydrotreating process. Based on these chemical changes it is reasonable that the partially hydrotreated pyrolyzate can be further processed at higher temperatures by more conventional hydrotreating techniques to produce hydrocarbon fuels.

TABLE 21. Components Identified in Low-Temperature Hydrotreated Pyrolyzate

Major*	Minor*
dimethoxyphenol (syringol)	methylcyclohexanol (2 isomers)
hydroxymethoxybenzoic acid	methylphenols (3 isomers)
propylsyringol	ethylphenols (2 isomers)
ethylsyringol	dimethylphenol
propylguaiacol	phenol
methylguaiacol	cyclohexandiol (2 isomers)
ethylguaiacol	methyltetralins (4 isomers)
methoxyphenol (guaiacol)	ethyl/dimethyl tetralins (2 isomers)
cyclohexanol	3 and 4 carbon substituted phenols (4 isomers)
	indan

* based on relative areas of flame ionization detector peaks, not strictly quantified.

Results of Catalytic Hydrotreatment of Low-Temperature Treated Pyrolyzate

Test results confirm the production of gasoline-range hydrocarbons from the low-temperature, catalytically-treated pyrolyzate. Catalytic hydrotreating conditions and processing results are nearly the same as those reported earlier for hydrotreating the TR12 high-pressure biomass liquefaction product.(3) In our continuous-feed reactor system, using sulfided cobalt-molybdenum catalyst, at conditions of approximately 350°C and 2000 psig, carbon conversion to gasoline was in excess of 80 weight percent. Product yield was somewhat less for the treated pyrolyzate compared to TR12 (0.77 ml/ml versus 1.0 ml/ml) due primarily to the higher oxygen content of the feedstock. The rate of conversion was slightly higher. Hydrogen consumption was measured at 728 liters per liter of oil feed (4085 SCF/bbl feed) based on gas phase measurements in and out of the reactor. Space velocity in our upflow reactor was relatively low (0.07 volume oil/volume catalyst/hr).

ACCOMPLISHMENTS

As a result of the last four years of research on hydrotreating biomass liquefaction products the following are identified as major accomplishments:

- The technical feasibility of catalytic hydrotreating high-pressure biomass liquefaction product to a gasoline-range hydrocarbon has been verified including the identification of appropriate catalysts and conditions,
- A process configuration has been formulated and tested to convert biomass flash pyrolyzate to gasoline via a low-temperature, catalytically treated intermediate,
- A series of phenolic model compounds have been tested and compared for relative activity toward catalytic hydrodeoxygenation,
- A series of hydrogenation and hydrotreating catalysts have been tested for relative activity toward hydrodeoxygenation of phenol,
- Two catalytic reactor systems were developed and tested in this hydrotreating research including a spinning-catalyst-basket, batch-charged reactor and a continuous-feed, fixed-bed reactor system.
- Results thus far indicate that product yields of 60 gallons of gasoline-range hydrocarbons per ton of dry wood can be obtained with TR7 (LBL-type) high-pressure liquefaction oil while 70 gallons of a combined gasoline-diesel range hydrocarbon are produced per ton of dry wood from the TR12 (PERC-type) oil. These yields are subject to improvement through the ongoing hydrotreating research efforts outlined in Future Research Plans as well as in the liquefaction research underway at other laboratories. Theoretical yields are in the range of 140 gallons of gasoline per dry ton of wood.

FUTURE RESEARCH PLANS

This report describes progress in an ongoing research project. Research topic areas have been identified which will receive further study. These topics include:

Mechanistic Determinations of Hydrotreating Wood Oil

Chromatographic analysis of intermediate products will be undertaken to identify reaction intermediates and discern the different reaction pathways affected by the different catalyst and processing conditions. Model compounds of functional types other than phenolics will be hydrotreated to determine reaction mechanisms.

Improved Catalysts

New catalyst formulations will be tested which are specially designed for use with heavy oils. These include multiple activity level catalyst beds and hydrocracking catalysts, i.e. metal-loaded zeolites. Longer-term tests will be undertaken to determine the extent of carbonaceous solid buildup in the reactor.

Improved Reactor Systems

The use of an ebullated bed in place of the fixed bed presently used will be investigated. Catalyst activity and carbonaceous solid buildup in the reactor bed may be alleviated by use of the ebullated bed. In addition, redesign of our reactor to an ebullated bed would allow more flexibility for product fractionation and recycle.

Development of Pyrolyzate Hydrotreating Techniques

Alternate means of producing more thermally stable pyrolyzates are also being investigated. Previous pyrolysis research has sought to maximize liquid phase product with little consideration of product quality. Future research will seek to produce pyrolyzates which can be directly hydrotreated.

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APPENDIX

EXPERIMENTAL REACTOR SYSTEMS AND ANALYTICAL PROCEDURES

EXPERIMENTAL REACTOR SYSTEMS AND ANALYTICAL PROCEDURES

Two reactor systems have been used in conducting this research. The initial tests with model compounds were performed in the batch reactor with a rotating catalyst basket. The processing of actual wood-derived liquids has been done in the continuous-feed reactor system which contains a fixed bed of catalyst pellets.

Batch Reactor System

Equipment Description - A catalytic reactor system has been developed which allows us to use commercial, pelletized catalysts in a batch-mode hydrogenation of phenolics. The reactor is shown schematically in Figure A.1. The unit is a one-liter, stainless steel, bolted closure autoclave. Our major modification has been the fabrication and insertion of a stainless steel mesh basket which holds the catalyst pellets. The basket turns with the stirring paddle which facilitates catalyst contact with the feedstock.

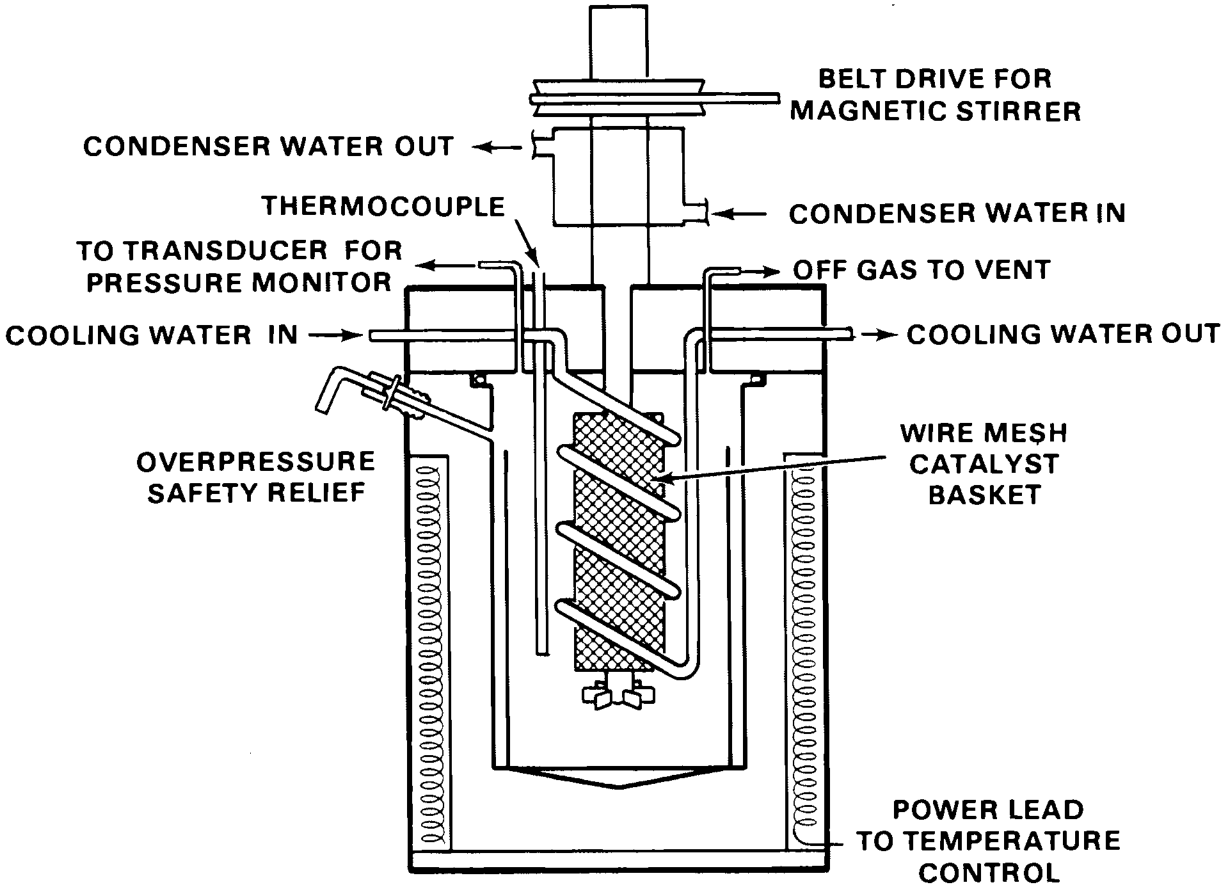

FIGURE A.1. One Liter Batch Catalytic Reacctor

The stirring paddle is the manufacturer's design which is designed to maximize gas contacting by drawing gas down through the hollow stirrer shaft and dispersing it into the feedstock with the stirring action. The standard stirring baffles have been removed and a stainless steel liner is used in the experiments. The reactor is externally heated.

Experimental Procedure - All reactants are added batchwise. The typical experiment involves addition of the feedstock into the liner, and the catalyst into the basket, after which the autoclave is sealed, purged and pressurized with hydrogen. The reactants are heated with stirring to temperature, held for a specified time, then quenched by the injection of cooling water through the coils in the interior of the reactor. The gaseous product is vented, the autoclave is opened and the products are recovered and analyzed. In a number of cases the hydrogen was nearly all reacted at the end of the experiment while substantial amounts of phenol remained unreacted. In these cases (as noted in the results section) the reaction environment was determined to be hydrogen limited.

Analytical Procedures - The liquid product recovered following the experiment was analyzed by gas chromatography in order to determine the product distribution. A 3% OV17 on 100/120 chromosorb WHP packing was used in a 6 foot by 1/8 inch nickel column. The carrier gas was helium at a flow of 31 cc/min. A flame ionization detector was used. The temperature in the column oven was programmed from 40°C to 250°C at 15°C/min with an initial hold time of four minutes. Figure 2 in the main text of this report presents a typical chromatogram obtained with this system. The peak identification was made by a combination of comparison with chromatographed standards and gas chromatography-mass spectrometry. Although a quantitative measure of the products was made there was no attempt made for a mass balance. Offgas analysis utilized a chromatography technique involving a Carle Automatic Gas Chromatograph configured to analyze Hydrogen Product Gas.

Continuous-Feed Reactor System

Equipment Description - In order to study catalytic hydrotreating of wood-derived liquids a continuous feed, bench-scale reactor system was assembled (see Figure A.2). Wood-derived oil, preheated to about 65°C, is pumped by a high-pressure metering pump. Hydrogen from a high-pressure cylinder is metered through a rotameter and mixed with the oil before they

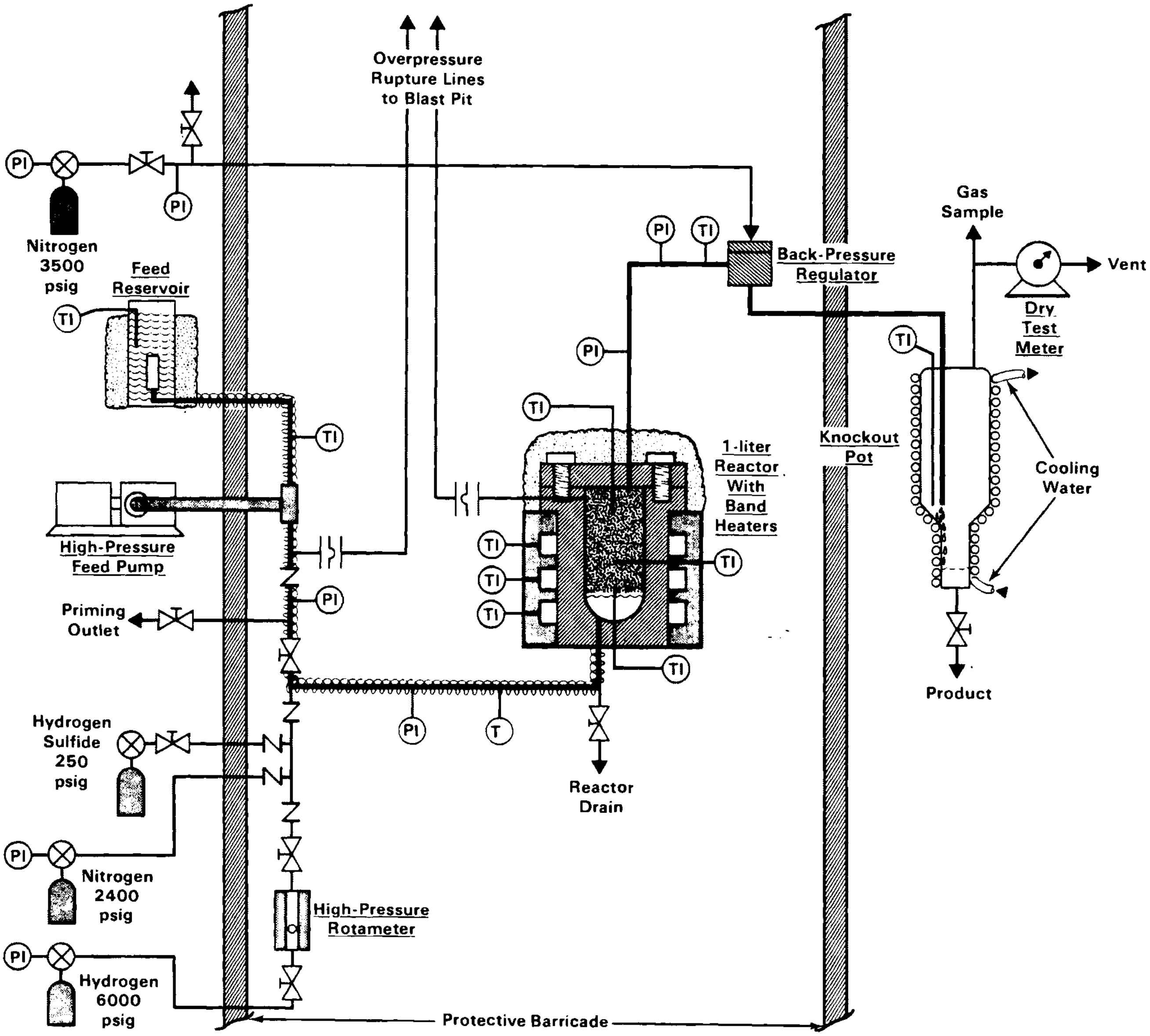

FIGURE A.2. Continuous Catalytic Hydrotreater

enter the reactor. The pressure vessel is approximately 7.5 cm I.D. by 25 cm high and holds about 900 ml of catalyst which is supported on a stainless steel screen. Void volume of the reactor when charged with catalyst is approximately 650 ml.

Our calculations indicate that for the liquid and gas rates used in our tests a two phase flow pattern exists in the reactor. Liquid moves through the reactor very slowly, essentially plug flow. Gas flows through more rapidly, bubbling through the oil. Light products are removed in the vapor phase with the hydrogen. There should be essentially no carryover of liquid with the gas until the liquid level reaches the top of the reactor and overflows into the product line. The pressure within the system is maintained by a back-pressure regulator (Grove valve). Condensed product is recovered from the offgas stream and the gas is metered and analyzed before it is vented.

Although petroleum hydrotreating systems generally are operated as down flow (trickle-bed) reactors, our experiments reported here were performed in an upflow system. The high molecular weight and polar nature of wood oil cause it to remain primarily as a liquid at operating conditions in contrast to petroleum-derived feedstocks which are used in a mixed phase with the bulk of the material in the gas phase. Our initial experience with the down flow system resulted in the outlet line being plugged with unconverted material. Similar results have been reported when hydrotreating coal pyrolysis tar.(1A) The use of the upflow reactor with either a fixed bed(2A) or a fluidized bed(1A) has been recommended as a means of achieving efficient catalyst contacting when operating with heavy feedstocks. In addition, the heavier, unconverted material is allowed additional residence time in the upflow reactor. In this manner the feedstock can be efficiently converted to light product without excessive cracking to gas or saturation of product because the light product leaves the reactor as vapor as it is formed.

The reactor can be operated in two basic modes. The reactor is started up at a high oil feed rate and a high quality, light product oil is removed overhead as a vapor along with the unreacted hydrogen gas. The light product outlet rate is less than the oil feed rate. The unreacted or partially reacted oil slowly fills up the reactor. The level in the reactor can be approximately determined by the temperature profile in the catalyst bed. As the liquid level approaches the top of the reactor two choices are possible:

1. Reduce the oil feed rate to the rate at which light products only are removed as vapors. A low oil feed rate is required to prevent overflow of liquid, incompletely converted product. This type of operation (Mode I) results in 100% conversion to light products and is sometimes referred to as extinction cracking.
2. Continue to feed oil at high rates which results in heavier liquid overflowing along with the light vapor product into the product receiver.

This results in production of a lower quality product but at much higher rates. This type of operation is referred to as Mode II.

Analytical Procedures - Detailed feedstock and product analyses were required to produce a mass balance for the experiments. Elemental analyses (carbon, hydrogen, nitrogen, and oxygen) were performed with Perkin-Elmer 240 and 240B microanalytical instruments which allow direct measurement of oxygen. Direct measurement of oxygen is important for the gasoline products wherein the oxygen is a minor component not accurately determined by difference. Elemental carbon measurements were also made on the aqueous by-products and the used catalysts. Moisture measurements in the feedstocks were made with a Karl Fisher automatic titrator with electrolytic reagent generation (Aquatest IV). Higher heating values of the products and feedstocks were measured in a Parr Adiabatic Bomb Calorimeter. Viscosities were measured with a Brookefield viscometer equipped with a small sample adaptor. Several types of distillations were used including the D1160 ASTM method for vacuum distillation, a short-path micro-distillation system and standard laboratory atmospheric distillations.

In addition to the general properties of the feedstocks and products, specific chemical component analysis was performed. Gas chromatography/mass spectrometry (GC/MS) was the primary means of obtaining identification of specific chemical components in the feedstocks and products. The chromatography was generally obtained with temperature programming from 50°C to 300°C on DB-5 or SE-54, 30 meter, wall-coated, open-tubular capillary columns. Qualitative information for identification of components was based on comparison of mass spectra with library spectra or by identification of the spectra directly in those cases where a standard spectrum was not available. Retention times were used as a secondary check to verify identities. Quantitation of components was made by gas chromatography using a flame ionization detector. Standard compounds covering a range of chemical functional groups and molecular weights were used to standardize the quantitation.

Besides GC/MS, chemical types were measured with infrared spectrophotometry (IR) and nuclear magnetic resonance spectrometry (NMR). Whereas the GC/MS analysis was only applicable to the chromatographable portion of the oils (lower molecular weight, less polar) the IR and NMR measurements were applicable to the entire product. Although the IR is not strictly quantitative for complex mixtures such as these, relative band intensities from one sample to the next can allow reasonable judgements as to changes in composition. The IR measurements were made with a Perkin-Elmer 283. Sample oils were pressed between salt plates and placed in the sample holder in order to make these non-quantitative measurements. The NMR measurements were made with a Varian FT-80A. This instrument has a tuneable probe so that both proton and carbon-13 spectra could be obtained. Quantitative measurements are produced by integration of the NMR signal and are used to measure the amount of specific functional group types, e.g. aromatic, aliphatic, phenolic, methoxyl, alcohol, or carbonyl, in the total oil mixture.

Product quality is judged in a number of ways. Three straight-forward measurements which provide the general characteristics of the product are the amount of oxygen in the product, the atomic ratio of hydrogen to carbon and the density of the product. It appears from our analyses of over 40 products and product fractions that the amount of oxygen and ratio of hydrogen to carbon (H/C) are inversely related in that products with lower oxygen usually have higher hydrogen to carbon ratios. Yet, the actual relationship between the two factors changes with the operating temperature and the catalyst type. The density of product, on the other hand, should probably be related directly to the oxygen content and H/C ratios by a rather simple function for all the products, but no numerical analysis has been attempted. The oxygen content and H/C ratios are inversely related as expected since the hydrogenation reactions would tend to decrease the oxygen content and increase the H/C ratios. The fact that the relationship between these two measurements varies at different temperatures and with different catalysts indicates that different types of hydrogenation reactions are being emphasized.

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