KINETIC STUDIES OF UPGRADING PINE PYROLYTIC OIL BY HYDROTREATMENT

A Dissertation

by

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ABSTRACT

Kinetic Studies of Upgrading Pine Pyrolytic Oil
by Hydrotreatment. (August 1985)

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The pyrolysis of biomass refers to incomplete thermal degradation resulting in char, pyrolytic oil, and gaseous products. The pyrolytic oil is a complex mixture of many components including phenolics, anhydrosugars, and polynuclear aromatics and is believed to have good potential as a liquid fuel. However, due primarily to its high oxygen content and high viscosity, the oil can currently be used only as a boiler fuel. An upgrading (hydrotreating) process is needed to improve the quality of the oil.

This research used pine pyrolytic oil produced by the Tech-Air Corporation from Southern Pine sawdust and bark. The hydrotreating reactions were conducted in a trickle bed reactor system. An analytical method combining size exclusion chromatography (SEC) and high resolution gas chromatography (GC) has been developed to analyze pine pyrolytic oil and its upgraded product. Changes in product composition as a function of experimental variables (reaction temperature, hydrogen pressure, space velocity and catalyst type) were determined quantitatively by comparing SEC–GC analyses and elemental analyses of the charged stocks and products. The catalysts used in the reactions were Pt/Al_2O_3, CoMo/γ–Al_2O_3, NiW/γ–Al_2O_3 and NiMo/γ–Al_2O_3. The reaction temperatures ranged from 623 K to 673 K, and the reaction pressures varied from 5272 kPa (750 psig) to 10443 kPa (1500 psig). Weight–hourly space velocity changed from 0.5 to 3.0 hr^{-1}.

Two models, one for overall oxygen removal and the other for the compositional changes in hydrotreated oil, were developed. Oxygen removal was not a function of space velocity and was modeled by an empirical function of temperature and pressure. A pseudo first order reaction network was used to relate the kinetic of a lumped model composed of five fractions. The lumps were determined by used of size exclusion chromatography – gas chromatography.

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TABLE OF CONTENTS

Table of Contents (Continued)

LIST OF TABLES

LIST OF FIGURES

List of Figures (Continued)

FIGURE Page

List of Figures (Continued)

CHAPTER I

INTRODUCTION

Biomass, which includes forest and agricultural products and residues, animal wastes, and municipal solid waste, is a renewable resource that could play a significant role in providing for future energy needs.

Biomass has the unique characteristic of being a renewable source of energy with a low concentration of impurities. This latter aspect is particularly favorable with regard to catalytic conversion processes in which the catalyst can easily be poisoned by impurities. Table 1 provides a general comparison of the physical and chemical properties of biomass and coal (Garten and Ushiba, 1980). Clearly there are marked differences which appear to favor biomass as a feedstock for synthetic fuels. The H/C ratio of biomass is very favorable, approaching values typical of petroleum-derived fuels. The conversion of coal to liquid fuel requires an increase in the H/C ratio by either the addition of hydrogen (hydroliquefaction) or the removal of carbon (pyrolysis). Conversion of biomass to liquid fuel, on the other hand, may be achieved by removal of oxygen.

The disadvantage of biomass is that the physical properties vary considerably, depending on the biomass resource, e.g., wood chips,

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rice hulls, straws and stalks. Such materials are not easily preprocessed by grinding to the small particle size attainable with coal.

Table 1. General comparison of biomass with coal

	Coal	Biomass
H/C*	0.2–0.8	~ 1.6
O/C*	0.007–0.25	~ 0.68
Ash*	7–12 wt%	0.2–3 wt%
S	0.8–3.4 wt%	Traces
N	1–5 wt%	~ 1 wt%
H_2O	Bit., ~ 2% Subbitum., ~ 10% Lignite, ~ 30%	Bark, ~ 10% ** Wood, ~ 10% ** Bagasse, ~ 50%

* dry basis.

** air dry.

A number of biomass thermal conversion processes are currently being developed, including combustion, gasification, and pyrolysis. Pyrolysis refers to incomplete thermal degradation which yields three major products: char (mostly carbon), oil (usable as a liquid fuel), and fuel gas (usable in any combustor). Conditions for biomass pyrolysis and products are somewhat dictated by reactor type and design. An excellent and detailed summary of biomass pyrolysis is given by Chatterjee (1981).

Although reported attempts at pyrolytic oil utilization are usually related to direct combustion, pyrolytic oil is a poor boiler fuel. It is viscous, not completely volatile, corrosive, exhibits high oxygen content, and does not mix with conventional fuels. Table 2 gives typical properties of No.6 fuel oil vs. Garret/Occidental's pyrolytic oil and Tech-Air's pyrolytic oil from pine sawdust and bark (Soltes, 1979). There is a striking similarity in the physical properties of the two pyrolytic oils produced through different processes. It should be noted that the Btu/lb for pyrolytic oil is considerably lower than that for No.6 fuel oil.

In order to improve pyrolytic oil as a liquid fuel, the oil must be processed to reduce viscosity, improve volatility, remove acidity, and lower oxygen content. A catalytic hydroprocessing reaction (hydrocracking and hydrotreating) was proposed to improve the quality of the oil. Catalytic hydrocracking can improve the yield of volatile feedstock. Reduction of oxygen content results in more hydrocarbon-like molecules of the higher energy content preferred in fuel. Hydrotreating can effectively lower the oxygen content, resulting in better fuels while usually promoting some cracking to enhance volatility.

Table 2. Typical properties of No.6 fuel oil and two pyrolytic oils

	No.6 Fuel Oil	Occidental Pyrolytic Oil	Tech-Air Pyrolytic Oil
C, wt.%	85.7	57.0	64.3
H	10.5	7.7	7.6
S	0.7–3.5	0.2	<0.01
Cl	–	0.3	–
Ash	0.05	0.5	<0.1
N	–	1.1	0.9
O	2.0	33.2	28.0
Density, g/ml	0.98	1.30	1.14*
Btu/lb.	18,200	10,600	10,600
Btu/gal.	148,800	114,900	119,000
Pour point,° C	18–29	32*	27*
Flash point,° C	66	56*	111*
Viscosity SSU at 190° F	340	1150*	–
cP at 25° C, Brookfield LV, 60 rpm	206	–	225*
Pumping Temp.° C	46	71*	–
Atomization Temp.° C	105	116*	–

* Pyrolytic oil contained 14% moisture

Pine pyrolytic oil obtained from pine bark and wastes by the Tech-Air pyrolysis process was used in this research. Earlier analysis of the Tech-Air pyrolytic oil (Elder, 1979; Elder and Soltes, 1979a; 1979b; 1980) indicated that solvent extractable phenolics comprise approximately 13 wt% of the oil. Pyrolytic oil also contains volatile organic acids, as well as a variety of neutral components (Soltes and Elder, 1981).

Figure 1 shows the gas chromatography - mass spectrometry (GC-MS) chromatogram of the Tech-Air pyrolytic oil (Sheu et al., 1984). Components identified by GC-MS are given in Table 3. The major volatile components (detectable by the gas chromatographic analysis) in the oil are the phenolics-phenol, cresol, some alkyl phenol, guaiacol, and eugenol. These studies show that pyrolytic oil is a complex mixture. A high percentage of the components of pine pyrolytic oil are relatively high in molecular weight. Less than 15 wt% of the pine pyrolytic oil can be detected by gas chromatography. The oil is very hygroscopic and has about 10 wt% moisture. Further, the oil is heat-sensitive and subject to re-polymerization, so it cannot be fractionated by distillation. The purpose of this research is to convert this heavy, high-oxygen-content oil into a lighter hydrocarbon mixture to obtain a better liquid fuel.

Because many species are contained in pyrolytic oil and its hydrotreated products, the lumping together of series of constituents with similar functional groups is a useful approach for showing the compositional changes in pine pyrolytic oil during the hydrotreating

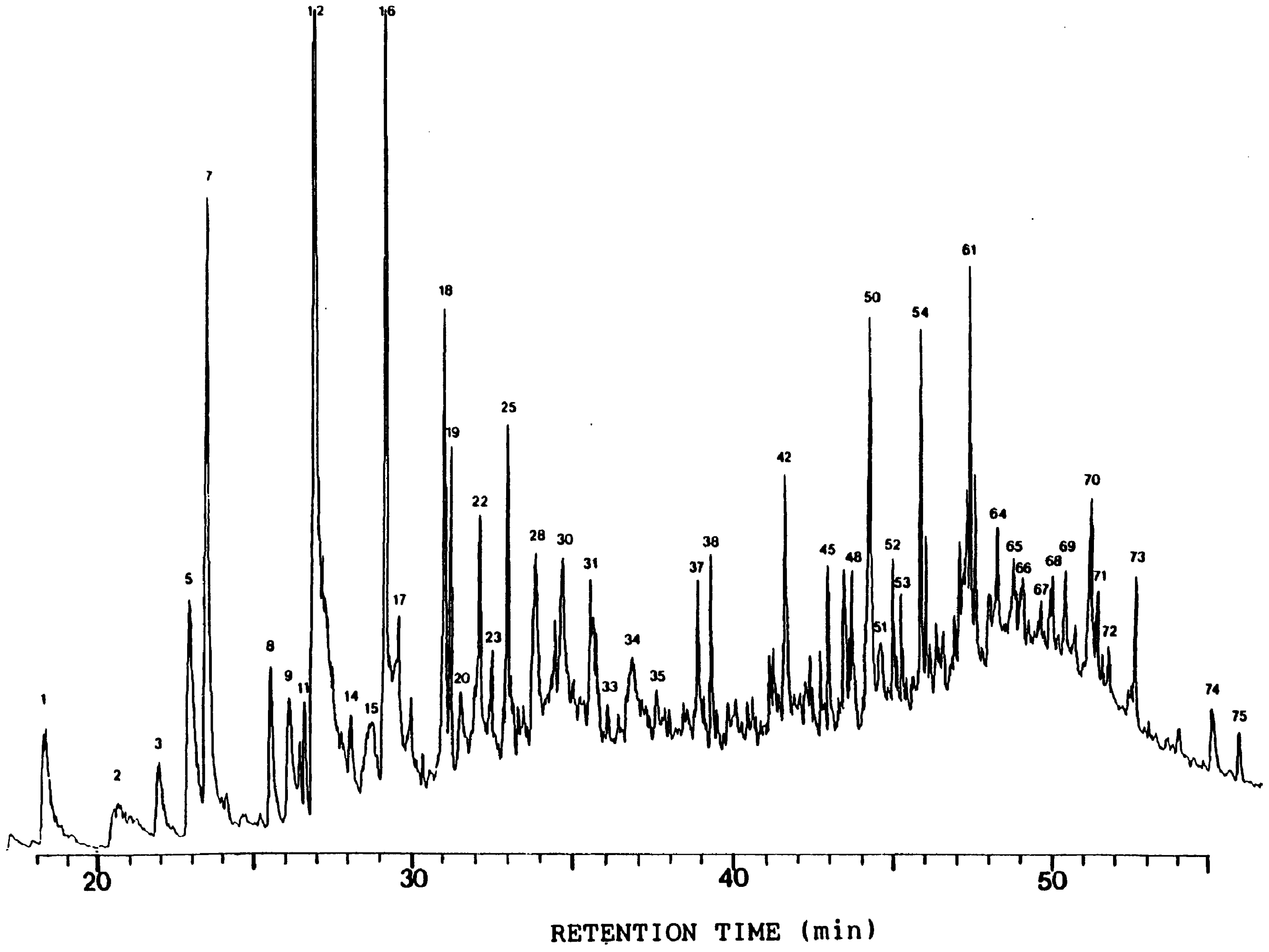

Figure 1. Gas chromatogram of pine pyrolytic oil. GC conditions: DB-5 fused silica capillary column, on-column injection, carrier gas: H_2, 25ml/min, temperature program, 30 to 100°C at 3°C/min, 100 to 280°C at 6°C/min. For peak identification see Table 3.

Table 3. Identified chemical components in pine pyrolytic oil (GC–MS without prior separation with SEC)

PEAK NUMBER	RETENTION TIME	% OF TAR	COMPOUND NAME
1	18.72	0.04	Phenol
2	21.25	0.0015	2–Hydroxy–3–methyl–2–cyclopenten–1–one
4	24.00	0.09	o–Cresol
5	24.03	0.22	m–Cresol + p–Cresol
6	24.60	0.39	Guaiacol
7	24.65	0.91	Guaiacol
8	26.88	0.30	2,4–Dimethylphenol
9	27.57	0.42	2,6–Dimethylphenol
10	27.95	0.15	6–Methylguaiacol
11	28.13	0.11	Naphthalene
12	28.50	3.28	4–Methylguaiacol
13	28.75	0.45	C_3–Alkylphenol
14	29.80	0.12	Dimethylguaiacol
15	30.40	0.022	C_3–Alkylphenol
16	31.05	1.32	4–Ethylguaiacol
17	31.52	0.049	Methylnaphthalene
18	33.15	0.79	Eugenol
19	33.38	0.39	4–Propylguaiacol
20	33.73	0.11	C_3–Alkylguaiacol
21	34.25	0.014	Vanillin
22	34.40	0.35	Isoeugenol
23	34.85	0.064	$C_{12}H_{20}$
24	35.28	0.034	Butylguaiacol
25	35.40	0.44	2–Methoxy–4–propenyl–phenol
26	35.80	0.034	C_4–Alkylguaiacol
27	36.32	0.15	Methyleugenol
28	36.38	0.43	Methyleugenol
29	37.10	0.052	Dibenzofuran
30	37.35	0.24	1–(4–Hydroxy–3–methoxy–phenyl)–2–propanone
32	38.58	0.028	Fluorene
34	39.65	0.010	Methyldibenzofuran
36	42.20	0.17	Guaiacylether

Table 3 (continued)

PEAK NUMBER	RETENTION TIME	% OF TAR	COMPOUND NAME
37	42.68	0.33	Phenanthrene
38	43.23	0.0044	Methoxyphenoxybenzene
41	44.93	0.090	Methylphenanthrene
42	45.37	0.11	Methylphenanthrene
46	47.50	0.021	2,3-Dimethylphenanthrene
47	47.68	0.027	$C_{19}H_{34}O_2$-ester
48	47.78	0.11	$C_{19}H_{34}O_2$-ester
49	48.25	0.065	1,1'-(1,2-Ethanediyl)bis-3,4-dimethylbenzene
50	48.43	0.55	9-Octadecanoic acid
51	48.78	0.018	C_3-Alkylphenanthrene
52	49.25	0.11	C_3-Alkylphenanthrene
54	50.27	0.29	1-Methyl-7-(1-methylethyl)-phenanthrene
59	51.75	0.084	1,1-bis(p-ethylphenyl)-ethane
61	52.02	0.21	$C_{21}H_{30}O_2$ ester
62	52.20	0.071	$C_{18}H_{32}O$ alcohol
63	52.68	0.010	$C_{21}H_{32}O_2$ resin acid, methyl ester
65	53.55	0.040	$C_{20}H_{28}O_2$
68	54.97	0.024	$C_{19}H_{40}O$ alcohol
70	56.33	0.26	$C_{20}H_{40}O_2$ fatty acid, methyl ester
72	57.00	0.030	$C_{21}H_{40}O_2$ fatty acid, methyl ester
73	57.95	0.090	$C_{22}H_{40}O_2$ fatty acid, methyl ester
76	65.10	0.66	$C_{26}H_{52}O_2$ fatty acid, methyl ester

reaction. It is rather ineffective to use the data based on physical and bulk properties such as viscosity, density, boiling point, and flash point for the monitoring of the fuel conversion process. Most workers in this area have used the differences in solubility of various components in different solvents (Baltisverger et al., 1977; Shultz and Mima, 1978; de Rosset et al., 1979) or adsorption chromatography (Jewell et al., 1972; Cogswell and Latham, 1977) on silica gel columns for the separation of petroleum and synthetic crudes. The major disadvantages of these techniques are the lack of material balance closure at the end of the separation and the time–consuming steps involved.

An analytical method combining size exclusion chromatography (gel permeation chromatography) (SEC) and high resolution gas chromatography (GC) has been developed to analyze pine pyrolytic oil and its hydrotreated product (Sheu et al., 1984). Earlier works show how SEC can be used to separate coal liquids, petroleum crude and its refining products into fractions based on 'linear molecular size' (Philip and Anthony, 1979, 1982; Philip et al., 1981). Since molecular linear size separation causes chemical species separation (similar chemical species happen to have similar molecular size), it is possible to separate chemical species such as alkanes, phenols and aromatics from complex organic mixtures such as coal liquids and pyrolytic oils. The separation method utilized the concept that SEC separates pyrolytic oil into fractions which are composed of only the following type of chemical compounds: nonvolatiles, alkanes, phenols, and aromatics. Gas chromatography (GC) with the use of an internal standard (1-decene) gives percentage of volatiles.

Only limited information is available on hydrotreatment of biomass-derived oils. All hydrotreating work on biomass pyrolytic oil to date has been done in batch reactors. Because of the long heat-up and cool-down periods in batch reactors, it is difficult to determine the reaction rate. Consequently, no kinetic data have been reported. To find the key reaction parameters and adjust them to obtain a high yield of desired product, a detailed kinetic study in a continuous reactor is needed.

In this research, a trickle-bed reactor is applied in the hydrotreating process. In a trickle-bed reactor, the liquid phase flows downward through a catalyst bed concurrently with the flow of the gas phase. Such reactors have been developed by the petroleum industry for hydrodesulfurization, hydrocracking, and hydrotreating of various petroleum fractions of relatively high boiling points. Among other advantages, the trickle-bed reactor offers a flow close to plug flow, allowing high conversion to be achieved in a single reactor. Also, the liquid flows as a film, thus offering very little resistance to the diffusion of the gaseous reactant to the catalyst surface. The hydrodynamics of trickle-bed reactors are quite complicated and have been studied extensively (Herskowitz and Smith, 1983; Shah, 1979).

The catalysts investigated in the reactions were Pt/Al_2O_3 (Strem, 78-166), $CoMo/\gamma\text{-}Al_2O_3$ (Harshaw, HT-400), $NiW/\gamma\text{-}Al_2O_3$ (Harshaw, HT-500), and $NiMo/\gamma\text{-}Al_2O_3$ (Harshaw, Ni-4301). The platinum catalyst was successful in upgrading pyrolytic oil in a batch reactor (Lin, 1981). The latter three were developed for petroleum hydrotreaters where the primary interest was in removal of sulfur or nitrogen heteroatoms. The reaction temperatures ranged from 623 K to 673 K, and the reaction pressures varied from 5272 kPa (750 psig) to 10443 kPa (1500 psig). Weight hourly space velocity changed from 0.5 to 3.0 hr^{-1}. The hydrogen to pine pyrolytic oil feed ratio was maintained at a constant value of $4.16*10^{-3}$ moles to 1 gram pyrolytic oil feed (640 cuft/ 1 barrel). The liquid feed was maintained at a constant ratio of 2 grams of decalin to 1 gram of pine pyrolytic oil.

Changes in composition during the hydrotreating process can be determined quantitatively, by comparing the SEC-GC analyses and the elemental analyses of the charge stocks and products.

The specific goals of this research were to:

1) Construct and test a laboratory trickle-bed reactor to study pyrolytic oil conversion rate. The pyrolytic oil was processed at varying conditions - H_2 pressure, reaction temperature, and space velocity - in order to kinetically relate oxygen removal and compositional change to processing conditions.
2) Evaluate hydrotreating catalysts (Pt/Al_2O_3, $CoMo/\gamma-Al_2O_3$, $NiMo/\gamma-Al_2O_3$, and $NiW/\gamma-Al_2O_3$) in the trickle-bed reactor.
3) Develop kinetic models linking the rates of compositional change and oxygen removal to the reaction conditions.

Although there has been much process research and demonstration activity in biomass pyrolysis, and although pyrolysis has been promoted as a biomass conversion process, there has been no implementation on a commercial scale. The major problem may be effective utilization of all three primary products, especially the pyrolytic oil. This research should impact the utilization of biomass as an alternative energy source for the production of liquid fuel.

CHAPTER II

LITERATURE REVIEW

In any biomass thermal degradation process - combustion, gasification, or pyrolysis - lignocellulosic materials first produce gases, liquids (tars), and solids (chars) as primary products. In combustion, excess air, elevated temperature, and long residence time result in complete oxidation of these primary products to uncombustible gases. In gasification, the temperature is somewhat lower and the air is sufficient to gasify the feed (through secondary reactions of tar and char products) but limited so that only partial combustion results. Combustible gases, mainly carbon monoxide and hydrogen, are produced. In pyrolysis, when biomass feed is subjected to short residence time at still lower temperature, and in the absence of air or under air-starve conditions, the primary gas, liquid, and char products do not undergo secondary reactions to any extent and can be recovered as final products. Conditions for biomass pyrolysis are somewhat dictated by conversion, reactor type and design (Soltes, 1979; Soltes and Elder, 1981; Chatterjee, 1981).

Depending on the process selected, liquid tar (pyrolytic oil) yield is variable but is generally 25 wt% of dry feed, such as reported for the Tech-Air pyrolysis process (Knight, et al., 1976). The pyrolytic oil is a complex mixture of organics and has potential as a feedstock for chemicals and fuels. An analysis of the Tech-Air pyrolytic oil derived from the pyrolysis of pine bark and sawdust (Elder and Soltes, 1979a; 1979b; 1980) indicated that solvent extractable phenolics comprise 13 wt% of the oil in which phenol, cresol, quaiacol, dimethyl phenol, alkyl guaiacol, and eugenol are the major components. Nonextractable, high molecular weight phenolics account for another 20 wt% of the oil. The oil also contains organic acids which are responsible for its corrosivity (Lin, 1978).

There are two approaches to pyrolytic oil utilization suggested by published studies: either some functional fraction such as the phenolics can be extracted and upgraded to some marketable product, or the oil must be chemically changed into a lighter hydrocarbon mixture to become a better fuel (Soltes, 1983a; 1983b). The phenolics in pyrolytic oil are currently being evaluated for their potential in adhesive formulations (Soltes and Lin, 1983a). This review will concentrate on upgrading of pyrolytic oil and oxygen removal by hydrotreatment.

Upgrading of Biomass Oil

Only limited information is available on hydrotreatment of biomass-derived oils. The use of platinum and other noble metal catalysts has been reported to result in hydrogenation of pyrolysis products to a gasoline-diesel mix (Lin, 1981).

Lin (1981) reports that catalytic hydrotreating and hydrocracking using noble metals as catalysts were successful in upgrading pine pyrolytic oil. He also reports results of a screening program using twelve catalysts in a batch reactor. Further studies suggested that

5% Pt and Pd powder catalysts in the presence of decalin solvent promoted more hydrocracking of C–O bonds and further reduction of large molecules. Lin's analysis showed that the raw oil was upgraded to a low-viscosity, low-oxygen-content, light liquid mixture of hydrocarbons, with increased heating value. The conversion rate of pyrolytic oil into liquid hydrocarbons by this process is above 50% on a weight basis and 85 to 90% on an energy basis. Noble metals on various supports will be used as catalysts to break C–O bonds (remove phenolic, hydroxyl and methoxyl substitutes), to saturate aromatics (leading to products of lighter color), and for hydrocracking (higher yields of liquid products with lower viscosities).

Hydrogen-donor solvents play a very important role in coal liquefaction. Hydrogen gas has been used in conjunction with the donor solvent either to help in hydrogenating the coal directly or to keep the donor supplied with available hydrogen. For upgrading biomass oil, hydrogen can serve as a reducing agent for removing oxygen. In Lin's report (1981), tetralin and decalin were used as solvents with 5% powder Pt on active carbon as catalyst. When tetralin was used, it was first hydrogenated to decalin, and decalin, rather than tetralin, was the effective hydrogen donor. Thus, the hydrotreated products contained only small amounts of tetralin and naphthalene ,and decalin was the predominant component. After this observation, decalin was used as a solvent and comparable results with lower hydrogen uptake were noted.

Lin concluded that the Pd catalyst plays a role not only in carbon-oxygen hydrogenolysis, which reduces oxygen content, but also in bridging between hydrogen, decalin, and pyrolytic oil to promote hydrogenation.

Elliott (1983) reported a catalyst screening of seven different commercial hydrotreating catalysts in hydrodeoxygenation of phenolic components of wood-derived oil in a one-liter autoclave reactor. The catalysts were CuCr, Pd (0.3%), Co, Ni, NiW, NiMo, and CoMo. The use of sulfided CoMo catalyst appeared to be preferred for hydrodeoxygenation of phenolics. The main products of the hydrogenation of phenol were benzene and cyclohexane. A number of dimers have also been detected in the product mixture. No results about upgrading actual wood-derived oil were given.

It was reported by Soltes and Lin (1983b; 1984) that both the pyrolytic oils (tars) from a variety of agricultural residues and their hydroprocessed products were indeed similar in compositions. Similar products were produced from Tech-Air pyrolytic oil, Dekalb corncob gasification tar, and the oils produced in a gasification/pyrolysis reactor from wood chips, rice hulls, cottonseed hulls, pecan shells, sugarcane bagasse, peanut shells, corncobs, and plywood trim. Compositions of catalytic hydroprocessed oils by a batch reactor were similar regardless of biomass feedstock used. Phenolics could be co-produced. The authors suggested that thermochemical conversion of physically dissimilar biomass feedstocks, followed by catalytic hydroprocessing of the oils (tars), might provide a universal route to useful oxychemicals and hydrocarbons from a variety of agriculture and forestry residues.

Oxygen Removal by Hydrotreatment

Extensive research activities in the area of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) during catalytic hydrotreatent of liquid fuels have been dictated by environmental concern to limit SO_2 and NO_x emissions. The sulfur and nitrogen content were lowered by hydrotreating, usually in a fixed bed or a trickle bed reactor at a hydrogen pressure in the range of about 7 to 14 MPa and temperatures in the range of about 573 to 673 K. Usually a catalyst of CoMo, NiMo or NiW supported on alumina or silica was employed and was presulfided *in situ*. Hydrodeoxygenation (HDO) has not attracted as much attention. This may be attributed to the very low amounts of oxygen found in conventional crudes, the main source of commercial fuels. Also, during HDO, the oxygen is removed in an environmentally harmless form.

Problems associated with the presence of oxygen arose as soon as synthetic liquids were identified as a potential source of commercial fuels. The content of oxygen in such liquids is sometimes an order of magnitude larger than that of sulfur and nitrogen. It is generally known that synthetic fuels containing large quantities of oxygen-containing compounds are rather unstable; for example, they quickly form deposits on exposure to air (Bowden and Brinkman, 1980). As a result of this, the unrefined synthetic liquids are usually a dark color.

Recent interest in oxygen removal by hydrotreatment is derived from efforts to upgrade heavy crude (Gorbaty and Harney, eds. 1979) or process coal-derived liquids into petroleum substitutes (Sullivan,ed. 1981). Catalyst development has been based on work of petroleum hydrotreaters where the primary interest was in the removal of sulfur or nitrogen heteroatoms. Catalyst combinations of nickel or cobalt with molybdenum or tungsten on alumina or silica supports are particularly useful.

Givens et al. (1979) studied the heteroatom removal from solvent refined coal as a function of temperature in the range of 390 to 450°C at 13871 kPa (2000 psig) pressure using sulfided $NiW/SiO_2 \cdot Al_2O_3$ catalyst. The data showed that the removal of sulfur, oxygen, and nitrogen increased as the reaction temperature increased. It was reported that on a relative gram-atom removal basis the number of oxygen, sulfur, and nitrogen atoms removed was in the order $O > N > S$.

Haider (1981) did a systematic catalytic hydrodeoxygenation (HDO) study of coal-derived liquid and related model oxygen-containing compounds. The studies were performed in specially adapted autoclave system using sulfided $CoMo/Al_2O_3$ and NiW/Al_2O_3 as catalysts. Starting feedstocks included: (a) 1-tetralone and 2-tetralone; (b) isochroman and 1,4-benzodioxan; (c) methyl benzoate; (d) phenol; (e) SRC-II middle-heavy distillate (b.p. 230-455°C). Comparison of these two conventional hydrotreating catalysts showed that the CoMo system had generally higher C-O hydrogenolysis activity and lower hydrogenation activity, whereas the NiW system had lower (aromatic) C–O hydrogenolysis activity and higher ring hydrogenation activity. Moreover, the latter catalyst had higher C–C hydrogenolysis activity. The results obtained with the model compounds and SRC–II distillate indicated that HDO of coal products was a slower and more complex process as compared to HDS and HDN of such products. Furthermore, C–O hydrogenolysis reaction in the presence of conventional sulfided catalysts not only proceeded at a slow rate, but also with low selectivity. They were accompanied by a variety of competing reactions leading to highly reactive intermediates which ultimately yielded coke and caused catalyst poisoning.

Simultaneous HDN and HDO of model compounds in a trickle bed reactor using NiMo as catalyst were studied by Satterfield and Yang (1983). In a binary mixture of a heterocyclic nitrogen compound and a phenolic or heterocyclic oxygen compound and in the presence of H_2S, the rate of HDO was considerably decreased in comparison to that observed with the same compound individually at the same reaction conditions. In the HDO of an ethylphenol, a substantial quantity of ethylcyclohexene was formed as an intermediate. The final products were ethylcyclohexane and ethylbenzene, the former predominating.

Kinetic data pertaining to HDO are limited compared to the information available on kinetic aspects of HDS and HDN of similar sulfur– and nitrogen–containing heterorings. Rollmann (1977) investigated the HDO rates of a series of model compounds at a temperature of 344°C and H_2 pressure of 5.0 MPa, over sulfided

$CoMo/Al_2O_3$ catalyst. A first order rate expression was used to calculate the rate constants. The 2,3-dihydrobenzofuran (DBF), benzofuran (BF), and o-ethylphenol were the most resistant to HDO and their rate constants were similar to those for HDN of quinoline and indole. The reactivities of p-cresol and 4-propylphenol were markedly higher. The HDO rates were affected by H_2 pressure, i.e., the rate constants increased with an increase in pressure.

Krishnamurthy et al. (1981) studied the kinetics of HDO of DBF and of related phenols (o-cyclohexylphenol and o-phenylphenol) at 343 to 376°C and 6.9 to 13.8 MPa H_2 pressure, and in the presence of sulfided $NiMo/Al_2O_3$ catalyst. It was assumed that all reactions were first order in the reactants. The rate constants increased with temperature but were independent of reactant concentration. The rate constants increased with increasing pressure.

A detailed kinetic study of HDO of a naphtha fraction obtained by direct liquefaction of coal was published by Ternan and Brown (1982). The work was performed in the temperature range of 300 to 500°C and pressure of H_2 ranging from 1 to 30 MPa in the presence of sulfided $CoMo/Al_2O_3$ catalyst. First order kinetics for HDO of this fraction was again assumed. The activation energy for the overall HDO, based on the experimental data was 84.8 kJ/mol. This value agrees with the activation energy for HDO of several model compounds reported by Krishnamurthy et al. (1981).

All three of the most popular commercial hydrotreating catalysts - $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, and NiW/Al_2O_3, plus Pt/Al_2O_3 were chosen to be the hydrotreating catalysts in this research to study the oxygen removal and conversion of pine pyrolytic oil.

CHAPTER III

EXPERIMENTAL

Feedstock

Pine pyrolytic oil produced by the Tech-Air Corporation from pine sawdust and bark was used in this research. The physical properties of Tech-Air pyrolytic oil are listed in Table 4. The purified grade decahydronaphthalene (decalin) from Fisher Scientific was used in this study as a solvent.

Catalyst

Details regarding the characteristics of the catalysts used in this research are given in Table 5. The 5% Pt/Al_2O_3 powder catalyst was mixed with Ludox AS-40 binder in such a proportion that the final catalyst contained 30% SiO_2. A paste was made when the binder was added. It was then taken into a syringe with a 1/16 inch (0.1588 cm) plunger. The catalyst was extruded, dried, and calcined in air at 756K (483°C) for four hours. In order to obtain an active catalyst, the Pt/Al_2O_3 pellet was reduced *in situ* prior to the experiments. The reduction was done by passing the H_2 through the catalytic bed at 673 K, 8720 kPa at a flow rate of 200 cm^3/min (21.2°C, 1 atm) for one hour.

For Harsaw's catalysts, the sulfided form was tested. Presulfiding of the catalysts was done *in situ* prior to the experiments. A mixture of 90% H_2 and 10% H_2S by volume was passed

Table 4. Properties of pine pyrolytic oil

Property	Result	Method
Density	1.1415 g/cm^3	
Water content	9.7%	ASTM D-85-70
Heating Value (wet basis)	27,800 KJ/Kg	ASTM D-240-64
Solubility (wt. %)		
Water	39.7%	
Acetone	99.6%	
Methylene Chloride	93.5%	
Toluene	slight	
Hexane	slight	
pH	2.9	5% oil dispersed in water
Filterable Solids (wt. %)	0.3%	Acetone insoluble
Acidity (milli-equivalents acid per gram of oil)	0.64	Titration by NaOH

Table 5. Specifications of the hydrotreating catalysts

Catalyst	Manufacturer	Size	Composition	Surface Area	Pore Volume	Pore Size diameter (Å)
Pt/Al_2O_3	Strem(78—166)	powder	5% Pt	$100\ m^2/g^*$	0.52 cc/g*	100*
CoMo	Harshaw(HT—400)	1/16" E.**	3% CoO, 15% MoO_3	$200\ m^2/g$	0.45 cc/g	94
NiMo	Harshaw(HT—500)	1/12" E.	3.5% NiO, 15.5% MoO_3	$200\ m^2/g$	0.46 cc/g	88
NiW	Harshaw(Ni—4301)	1/12" E.	6% Ni, 19% W	$230\ m^2/g$	0.37 cc/g	104

* For the pellet catalyst.

** E: Extrudates.

through the catalyst bed at a flow rate of 40 cm^3/min (measured at 21.2°K, 1 atm) at 673 K and and atmospheric pressure until the outlet gas showed no further sign of H_2S consumption.

Apparatus

In this study, a trickle-bed reactor was constructed for catalytic hydrotreating, primarily because it has been widely used in the petroleum industry for hydroprocessing. It is designed to fulfill the following requirements:

1) The reactor operating pressure must be controlled up to a maximum of 13,891 kPa (2000 psig).
2) The reactor should be capable of operation at temperatures up to 700 K.
3) The flow rates of the pyrolysis oil, solvent, and hydrogen must be measured and controlled accurately.
4) Continuous operation must be possible.

The schematic process of a trickle-bed reactor system is shown in Figure 2. The system can be divided into the following sections:

1) Liquid feed system:

   A high pressure metering pump (Lapp, MLS-20) was used to pump the liquid feed which is the mixture of pyrolytic oil and decalin solvent.

2) Gas feed system:

   Reactant hydrogen was supplied by a high pressure cylinder. A cylinder of nitrogen gas was also connected for flushing out the

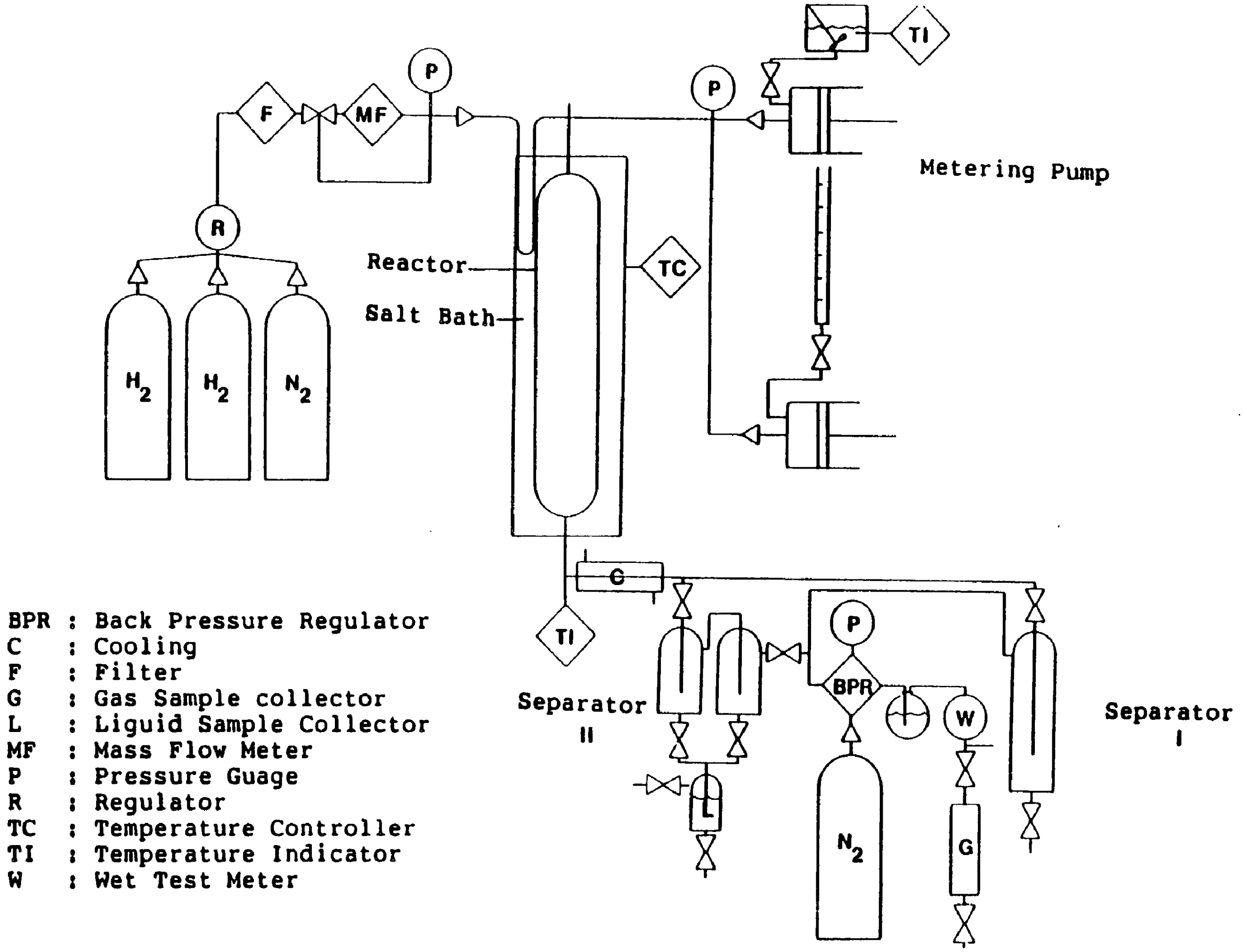

Figure 2. Schematic process of trickle-bed reactor system

system. A thermal mass flow meter (Brook's, Model 5810 1F1A) with an automatic control valve was used to control and measure the hydrogen flow rate.

3) Trickle bed reactor:

The structure of the reactor is shown in Figure 3. The reactor consists of a 316 stainless steel tube of 3/4 inch (1.905 cm) O.D. and 0.065 inch (0.1651 cm) thickness. The top 20 inches (50.8 cm) of the reactor was packed with catalyst and the bottom 12 inches (30.48 cm) was packed with Pyrox® 3 mm diameter glass bead (Cat. No. 7268-3) as the inert support. The reaction temperature was nonisothermal by immersing 22 inches (55.88 cm) of the reactor in a salt bath as shown in Figure 3.

4) Salt Bath and Temperature Control:

The salt bath was made from five inch O.D. (12.7 cm) cast iron tube thirty four inches (86.4 cm) long with an expansion at the top and bolted flanges at the bottom. An automatic temperature controller (Techne AC-40) was used to control the temperature of the salt bath. The heating medium used was a Hitec® heat transfer salt which is a mixture of 53% potassium nitrate, 40% sodium nitrite and 7% sodium nitrate (American Hydrotherm Co.). Two semi-cylindrical unit heaters from Watlow (Model VS 05A 240A) were used to heat the salt bath. A type K temperature probe (chromel-alumel) was inserted into the salt bath to measure the salt bath temperature. Air was bubbled through the salt bath to ensure a more uniform temperature profile.

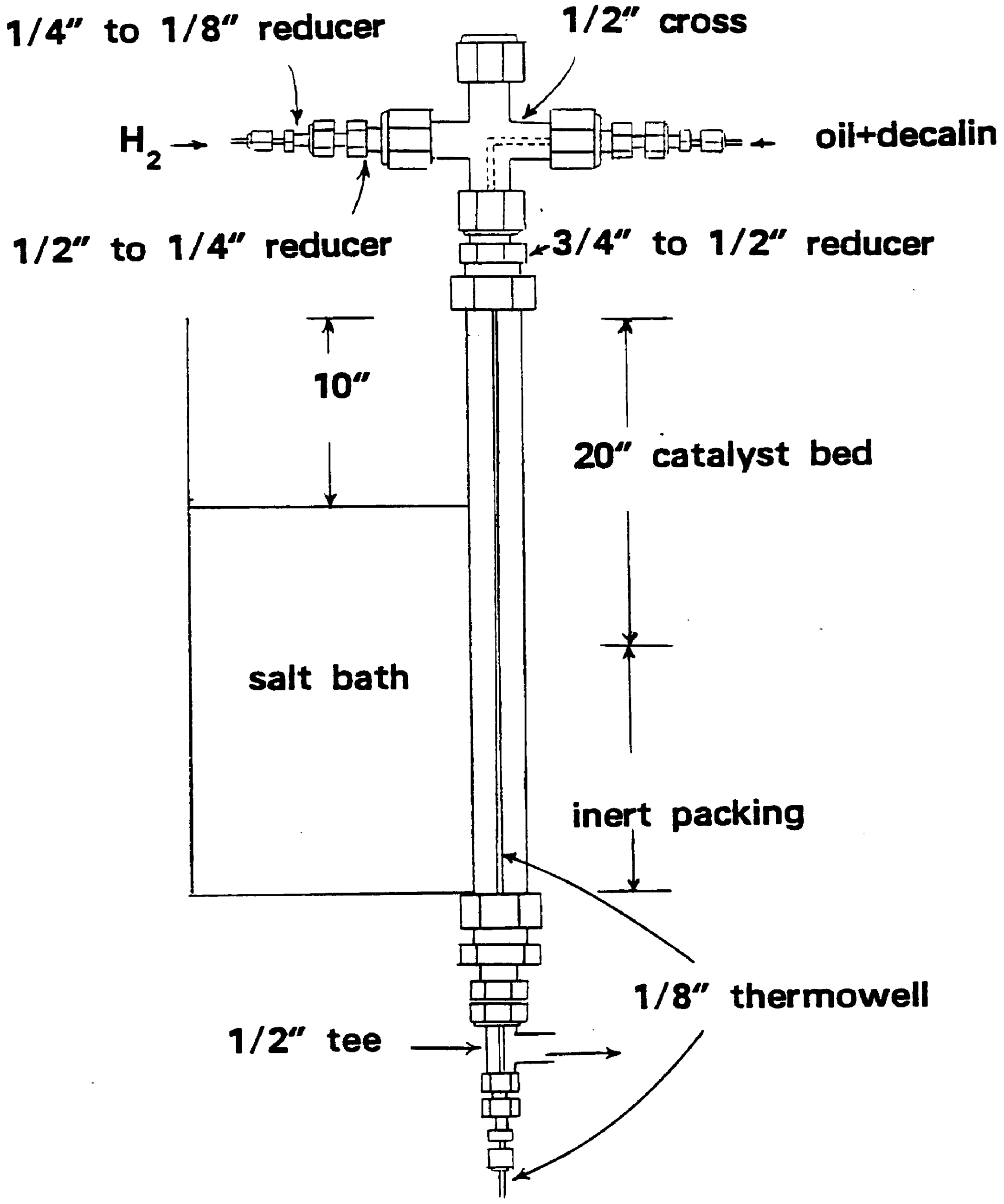

Figure 3. Trickle-bed reactor

5) Gas liquid separation and sampling:

As shown in Figure 2, the exit stream from the reactor was introduced into two different sizes gas–liquid phase separators. The separator I was an one liter high pressure vessel. The separator II was composed of two 100 cm^3 sample bomb. A liquid sample collector was connected at the bottom of the separator II. The gas then passed through a back–pressure regulator (Grove, Mity Mite 5–91 XW), to reduce the outlet stream pressure from system pressure to atmospheric pressure. The pressure in the back–pressure regulator was set by a nitrogen cylinder at the designed reaction pressure. The outlet gas passed through a water saturator and a wet test meter to measure the outlet gas flow rate. The outlet gas from the wet test meter was then passed through a union–tee with septum where a gas sample could be taken with a gas syringe for analysis. The liquid phase was collected in a cylinder for later analysis.

The whole system was designed to have a maximum working pressure of 13,891 kPa (2000 psig). Type 316 Stainless steel had been selected for all tubing, fitting, valves, and vessels.

Experimental Procedure

The trickle–bed reaction system was arranged to feed liquid and gas reactant accurately through the catalyst bed. The pyrolytic oil and decalin were first mixed in a closed tank at a weight ratio of 2:1 and heated to 353 K (80°C) before being pumped by a high pressure metering pump. The outlet stream from the pump passed through a check valve preventing back flow of the liquid due to high pressure inside the reaction. The liquid was preheated with a heating tape at 190°C and then fed into the reactor. The gas flow rate was measured and controlled by the mass flow meter. The hydrogen was preheated through coils inside the salt bath before it was fed into the reactor. Table 6 shows typical operating conditions.

Table 6. Typical reactor operating conditions

Gas Feed (H_2) : 100 cc/min (at 60°F, 1 atm) per gram of pine pyrolytic oil input.

Liquid Feed : at a ratio of 2 grams decalin per gram of pine pyrolytic oil

Weight Hourly Space Velocity (WHSV)* : 0.5 to 3.0 hr^{-1}

Salt Bath Temperature : 623 to 673 K

H_2 Pressure : 5,272 to 10,443 kPa (750 to 1500 psig)

Catalyst Bed : 60 grams for each load

$$^{*}\text{WHSV} = \frac{\text{Gram of pine pyrolytic oil input per hour}}{\text{Gram of catalyst in the reactor}}$$

The gas and liquid were fed concurrently from the top of the reactor. A 1/8 inch (0.3175 cm) thermowell was extended from the bottom to the top of the reactor. A 0.04 inch (0.1015 cm) OD chromel-alumel thermocouple (Omega Model 4001KC1) was inserted into the thermowell and moved up and down to measure the axial temperature profile of the reactor during the reaction. Figure 4 shows two typical temperature profiles inside the reactor at two different salt bath temperature settings.

By immersing 22 inches of the reactor in the salt bath, the temperature inside the reactor increased gradually along the reactor length. This prevented the volatiles in the pine pyrolytic oil from flashing into the gas phase suddenly. With the catalyst packed at the top section of the reactor, the pyrolytic oil was hydrotreated before the oxygen-containing compound polymerized at high temperature.

During the experiments, except for collecting liquid sample for analysis, the gas and liquid products from the reactor were cooled and separated in gas-liquid separator I. The liquid samples were collected according to the following procedure. First, close the valve between the reactor and separator I, and open the one between the reactor and separator II. The reaction products were cooled and separated in separator II. The liquid sample collecting time, depending on the liquid feed rate (WHSV), was between 2 to 8 minutes. Then, switch the product stream back to the separator I. The valve between separator II and the liquid sample collector was opened and the liquid drained into the collector. The pressure of the system fluctuated only to an amount to raise the liquid sample collector to the system pressure. Then, the valve between the separator II and

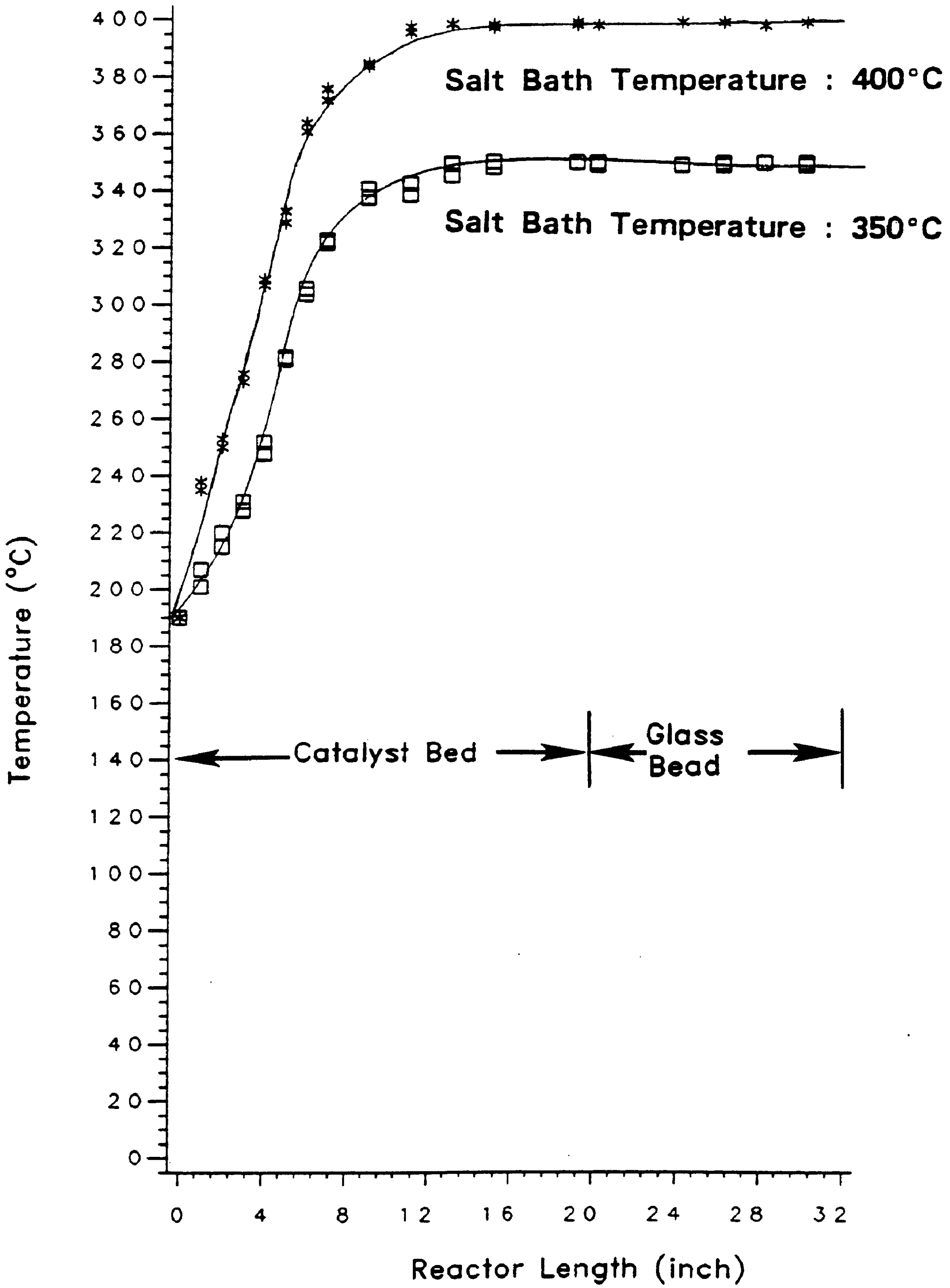

Figure 4. Temperature profile inside the reactor. Reaction conditions: Pt/Al_2O_3 catalyst, 8720 kPa, WHSV = 2 hr^{-1}, salt bath temperatures: 623 K (350°C) and 673 K. (400°C)

collector was closed. The pressure in the liquid sample collector was first released through the valve at the top slowly and the liquid sample was withdrawn by opening the outlet valve at the bottom of the collector. The products collected in the separator I were discarded after the experiments. The product gases were passed through the back pressure regulator to reduce the pressure to atmosphere pressure. The outlet gases passed through a water saturator and a wet test meter to measure the gas flow rates.

Regeneration Experiment

The catalyst regeneration consists in the calculation and removal of the coke deposited on the catalyst during the reaction by burning the coke with air. In these experiments, the reactor was heated to 673 K. A constant flow of nitrogen (500 cm^3/min) at atmospheric pressure was passed through the catalyst bed for 1 hour to flush out the liquid and H_2 which was adsorbed on the surface of catalyst. Then, a constant flow of air (500 cm^3/min) was fed into the reactor. The regenerations were performed at a pressure of about 650 kPa in order to maintain a high partial pressure of oxygen. The outlet stream bypassed the separators and went through the back pressure regulator to the ice-traps. The reactor effluent was analyzed and the exit gas flow rate measured using the wet test meter. The water collected in the ice trap was weighed.

In this experiment trace amounts of hydrocarbons were liberated during the first minutes of reaction. During reaction the oxygen present in the air reacts with the coke on the catalyst to produce carbon dioxide and water. After some time, the coke is depleted and the oxygen concentration increases to the concentration of air, indicating the completion of the regeneration. Figure 5 shows a typical result for the regeneration experiments.

The total amount of coke deposited on the catalyst during reaction was calculated from the total amounts of carbon and hydrogen that exited the reactor during regeneration in the form of CO, CO_2, H_2, water, and hydrocarbons. An integration of the flow rate of the gas products, such as CO_2, CO, and CH_4, gave an indication of the amount of coke deposited on the catalyst.

After the regeneration experiments, the catalyst bed was activated again for the next run. For Pt/Al_2O_3 catalyst, H_2 was passed through at 673 K and 8720 kPa for activation pretreatment. CoMo, NiMo, and NiW catalysts were resulfided at 400°C and atmospheric pressure in the presence of a flowing stream of H_2 containing 10% H_2S.

Sample Analysis

Gas Sample

The gas sample was analyzed using a Carle Series S, 111 H analytical gas chromatograph, with columns and programs as reported by Philip, Bullin and Anthony (1979). A Hewlett-Packard 3385A Automation System integrator and printer was used in conjunction with this GC. By knowing the flow rate from the wet test meter, the outlet gas composition from the reactor was determined on a mole basis.

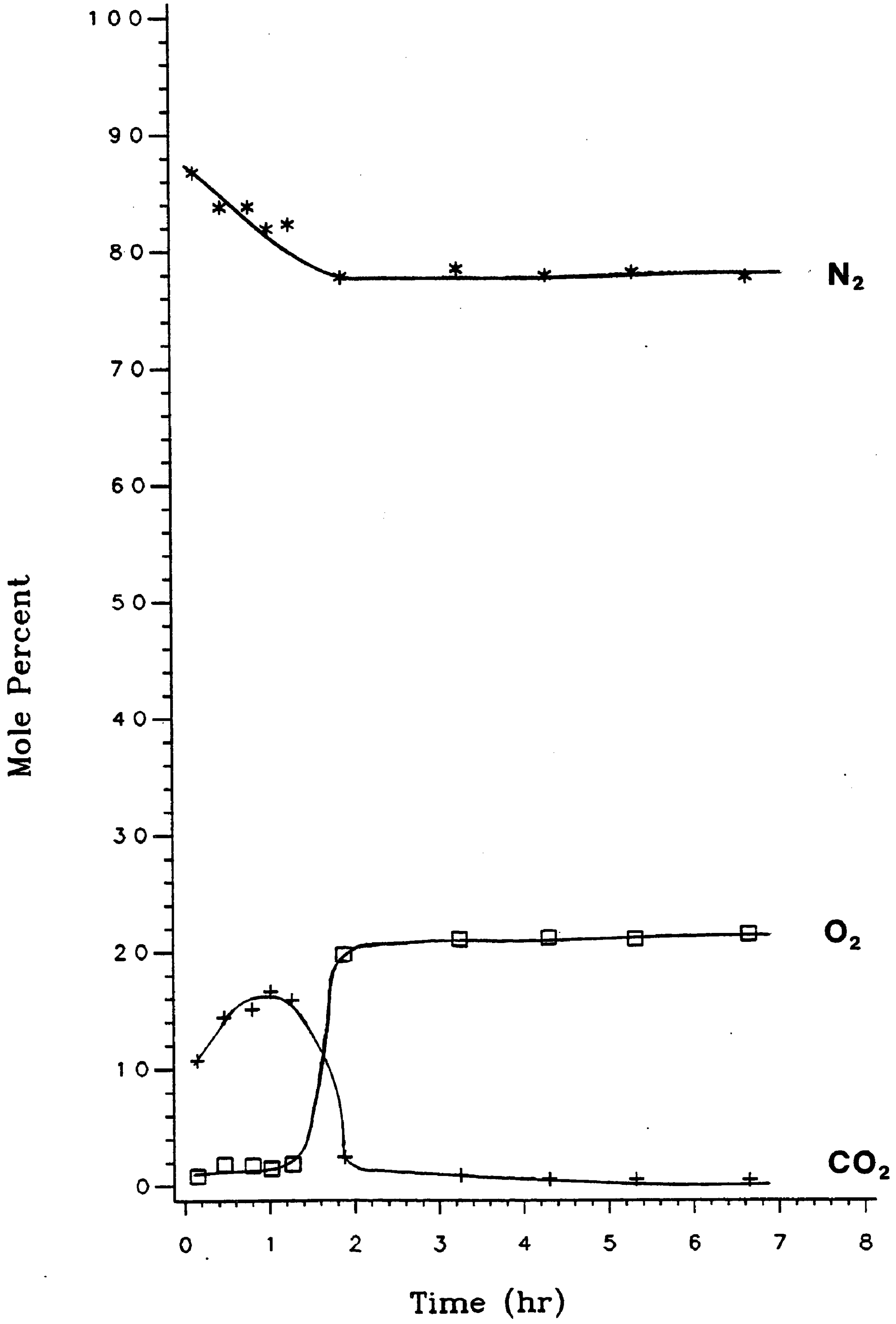

Figure 5. N_2, O_2, and CO_2 product compositions on a water free basis for a typical regeneration experiment.

Liquid Sample

Gas chromatography (GC) is suitable for analysis of the volatiles of pyrolytic oil and its hydrotreating product, but it cannot be used for analysis of the nonvolatile components. Size exclusion chromatography (SEC) can be used for the separation of functionalities in oil, both volatile and nonvolatile (Sheu et al., 1984). The SEC separations were performed on a Waters Associate Model ALC/SEC 202 liquid chromatograph equipped with a refractometer (Model R401). A 5nm μStyragel column (7.8mm I.D., 60cm long) was used. Tetrahydrofuran (THF), refluxed and distilled with sodium wire under a nitrogen atmosphere, was used as the mobile phase in the SEC. The flow rate was 1 ml per minute.

All samples were filtered using micropore filters (Millipore, pore size=0.5 μm) before injection into the SEC column. Because the crude pyrolytic oil was very viscous, a 25% solution of oil in THF was used. The maximum injection volume was 250 μl. The pyrolytic oil samples separated by SEC were divided into four or five fractions, which were collected in glass vials. The vials were warmed on a hot plate while a slow dry stream of nitrogen swept through the vials (but not bubbling through liquid phase). During the procedure the temperature of the contents of the vials was below 323K (50°C) but complete removal of THF was possible. The glass vials with the contents were weighed to constant weight to ensure the complete removal of any SEC solvent. The weight of pyrolytic oil fractions in each vial was determined. For some GC analyses the fractions were concentrated without removing THF completely in order to detect some low boiling point components such as toluene and xylene although their analysis were not quantitative. Prior to GC analysis, a known amount of 1-decene was added as an internal standard.

The separated fractions were analyzed using a Tracor 560 GC system with microprocessor-assisted temperature programming capabilities and a flame ionization detector (FID). The GC data were saved and integrated by an IBM-Instruments 9000 computer. The GC-MS analyses were performed by a Hewlett-Packard 5985A system. A DB-5 fused-silica capillary column with an immobilized methylsilicone phase (J&W Co.) was used in GC and GC-MS for characterization work. A 12 foot glass column packed with 10% SP-2100 on 100/80 Supelcoport was used to estimate the volatiles which is defined as the total amount of components detected by FID and calculated using an internal standard method and relative response factors for different species. The response factor (RF) which is used for the calculation is expressed by the following equation:

$$RF=[area\%(sample)/wt\%(sample)]*[wt\%(STD)/area\%(STD)].$$

The response factors for fraction 2 (alkanes) and fraction 4 (aromatics) are assumed equal to one which agree with with the value reported by Dietz (1967). The RF for fraction 3 (phenols) is 0.75 which is the average value of seven major phenols in pyrolytic tar related to SP-2100 packed column.

Changes in composition during the hydrotreating process can be determined quantitatively, by comparing the SEC-GC analyses and of the charge stocks and products. This separation scheme is quite appropriate for studying the chemical transformations that occur on hydrotreating of pyrolytic oil in which the production of aromatics occurs as oxygen are removed from the more polar molecules.

CHAPTER IV

RESULTS AND DISCUSSION

The experimental data using Pt/Al_2O_3, CoMo/Al_2O_3, and NiMo/Al_2O_3 catalysts are listed in Appendix A. The experimental data include reaction conditions, material balances, and analytical data by the SEC–GC method. No NiW/Al_2O_3 data are included. During all NiW/Al_2O_3 reactions, significant coke was formed which plugged the reactor and gradually increased the system pressure.

The inputs in the material balances include liquid feed (pine pyrolytic oil plus decalin) and hydrogen gas feed. The hydrogen to pine pyrolytic oil feed ratio was maintained at a constant value of $4.16*10^{-3}$ moles to 1 gram pyrolytic oil feed. The liquid feed was maintained at a constant ratio of 2 grams of decalin to 1 gram of pine pyrolytic oil. The outlet includes liquid product (excluding the water layer), outlet gas, water (water layer in liquid product), and coke deposited on the catalyst. The material balances were calculated based on one gram of pine pyrolytic oil plus two grams of decalin feed. The carbon, hydrogen, and oxygen composition in the hydrotreated oil was determined by elemental analysis. A sample calculation is given in Appendix B. The outlet gas was measured by wet test meter and its composition determined by GC analysis. The coke determined by the regeneration experiment represents the accumulated amount of coke that had been deposited on the catalyst during the run. The amount of gas and coke shown in the material balance are the total amount divided by the total pyrolytic oil input. The amount of H_2O is determined by separating and weighing the water layer in hydrotreated pyrolytic oil.

Also listed in Appendix A is the analytical results of hydrotreated pyrolytic oil by SEC–GC analysis. The weight percentage (based on one gram of pine pyrolytic oil input) of each fraction and its volatility are included. The details of the SEC–GC data will be discussed later in this chapter.

Oxygen Removal

The amount of oxygen, in pine pyrolytic oil and its hydrotreated products, was determined by elemental analysis. First, the carbon and hydrogen weight percentages of the whole hydrotreated pyrolytic oil were obtained through elemental analysis. Then, the carbon and hydrogen contributed by the solvent (decalin, tetralin, and naphthalene) were subtracted. The weight of oxygen in hydrotreated oil (excluding solvents) per gram of pyrolytic oil input is listed in Appendix A. A sample calculation concerning the determination of oxygen concentration is listed in Appendix B.

The effect of reaction temperature, pressure, and space velocity are shown in Figures 6 through 8. The points in the Figures are the experimental data and the solid line were evaluated from an oxygen removal model which will be discussed in details as follows. A clear trend of the effect of reaction temperature and pressure on the oxygen removal in the hydrotreating process can be observed in Figures 6 and 7. Figure 8 shows that the changes in space velocities did not affect oxygen removal.

Even though the oxygen removal was not a function of space velocity, equation (1) is used because of the temperature profiles and pressure dependence on the experimental data. An Arrhenius type equation and an nth order pressure effect are assumed in equation (1).

$$\frac{dX_{oxy}}{dZ} = K\, C^{m}_{oxy}\, P^{n} \tag{1}$$

where:

C_{oxy} = concentration of oxygen in pyrolytic oil.

$$= \frac{\text{gram of oxygen in hydrotreated oil}}{\text{gram of oxygen in raw pyrolytic oil.}}$$

K = $A\ e^{-E/RT}$

P = reaction pressure.

m = reaction order.

n = nth order pressure effect.

X_{oxy} = oxygen conversion.

Z = reactor length. Inserting $dC_{oxy} = -C^{o}_{oxy}\ dX_{oxy}$ into equation (1), the corresponding integrated equation becomes:

$$\frac{(C^{(1-m)}_{oxy} - 1)}{m - 1} = C^{o}_{oxy} \int_{o}^{Z_T} K\, P^{n}\, dZ \tag{2}$$

where:

C^{o}_{oxy} = initial oxygen concentration (equal to one).

Z_T = total catalytic bed length.

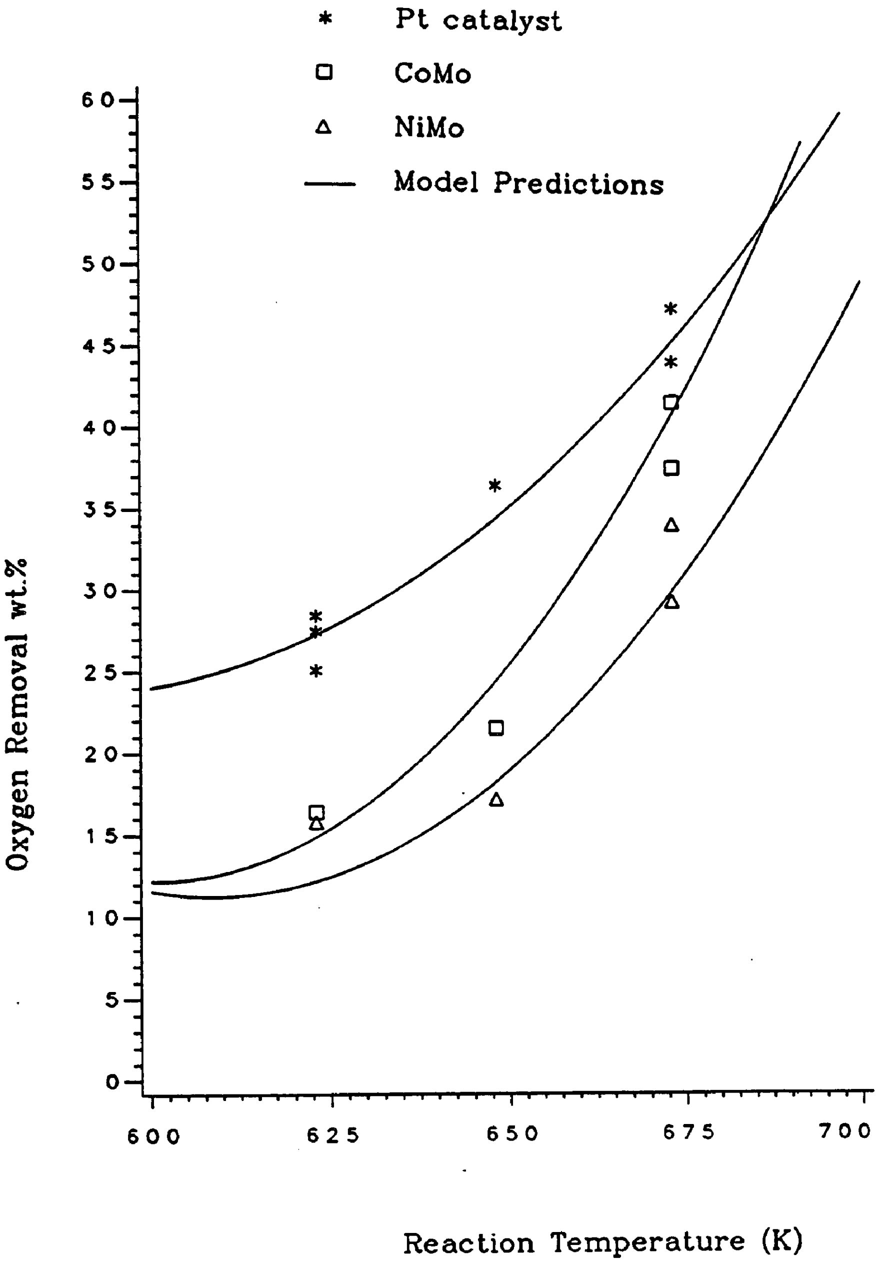

Figure 6. Temperature effect on oxygen removal during the hydrotreating process. Pressure: 8720 kPa, WHSV: 2 hr^{-1}.

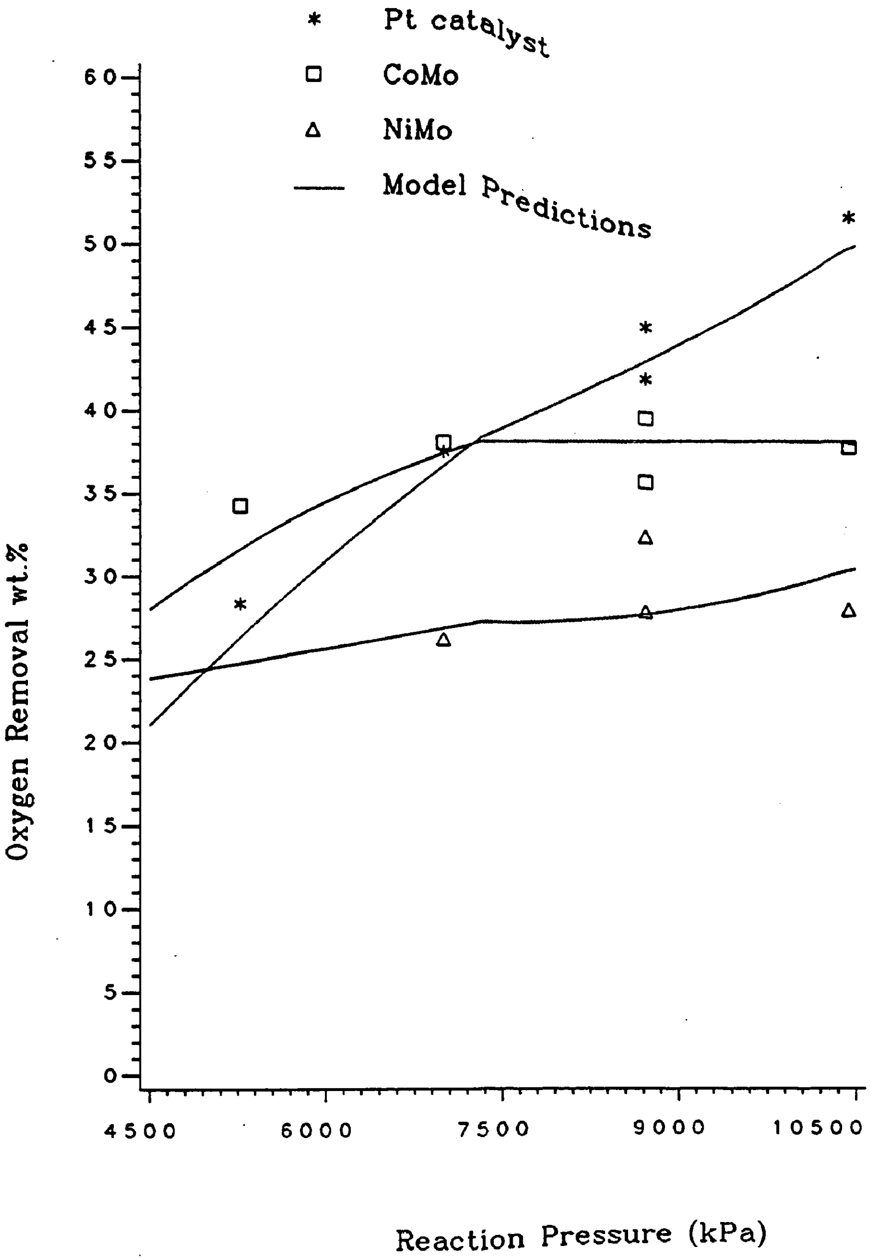

Figure 7. Pressure effect on oxygen removal during the hydrotreating process. WHSV: 2 hr^{-1}, temperature: 673 K.

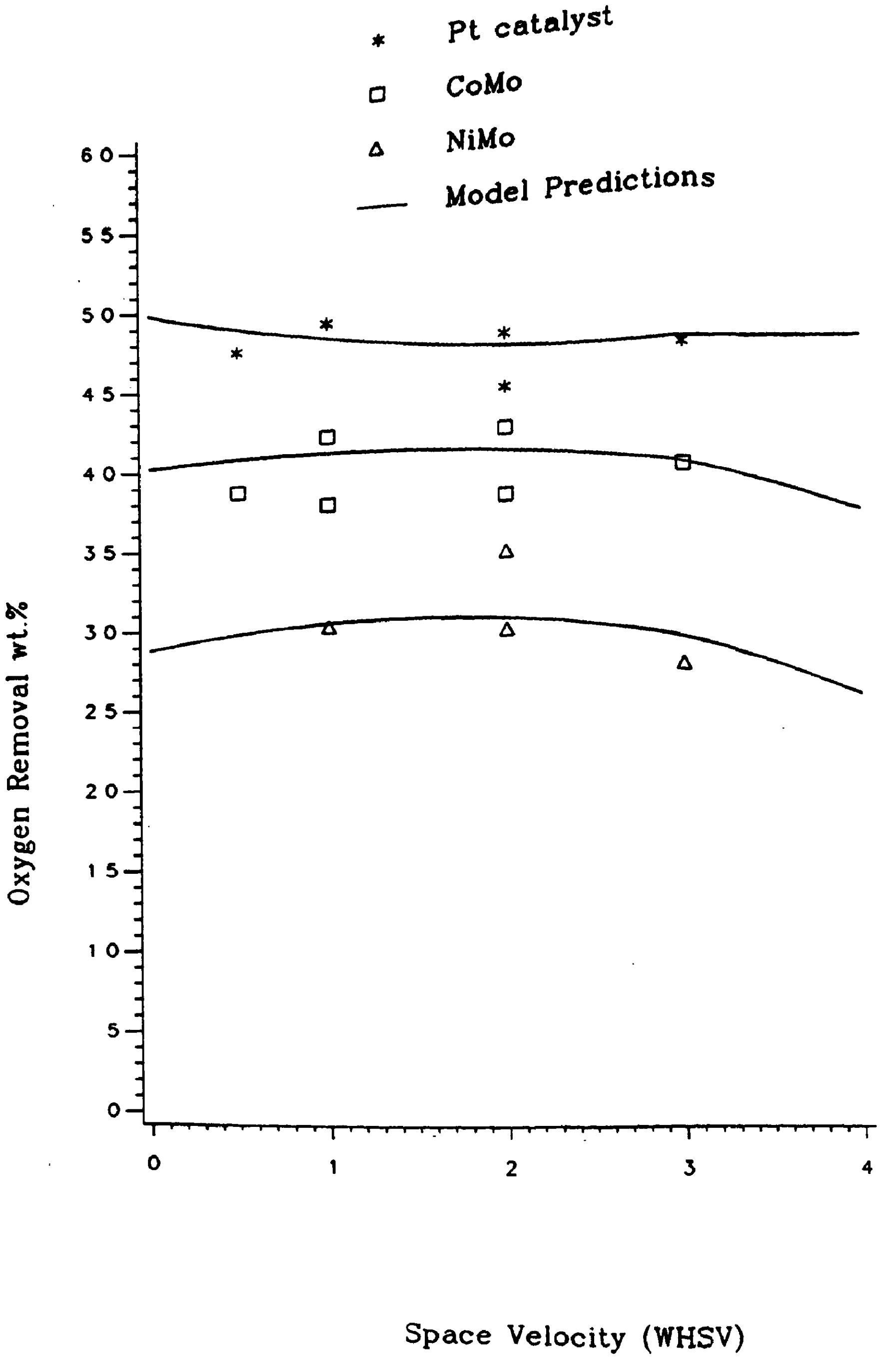

Figure 8. Space velocity effect on oxygen removal during the hydrotreating process. Pressure: 8720 kPa, temperature: 673 K.

Since all the reactions were run at nonisothermal conditions and axial temperature profiles were measured (T=T(z)), the K, is

$$K = K_o \exp\left(\frac{E}{RT_o}\left(1-\frac{T_o}{T(z)}\right)\right) \tag{3}$$

where K_o is evaluated at reference temperature T_o (648 K), and E is the activation energy.

Hence, equation (2), can be written as:

$$\frac{(C_{oxy}^{(1-m)} - 1)}{m - 1} = C_{oxy}^{o} P^{n} \int_{o}^{Z_T} K_o \exp\left(\frac{E}{RT_o}\left(1 - \frac{T_o}{T(z)}\right)\right) dZ \tag{4}$$

The integral $I = \int_o^{Z_T} K_o \exp(E/RT(1 - T_o/T(Z)))\, dZ$ was evaluated at six different reactor lengths (Z_1, Z_2, Z_3, Z_4, Z_5, Z_6) between 0 and Z_T as given by the Gauss Quadrature numerical technique. The six point Gauss Quadrature constants are as follows:

$w_1 = w_2 = 0.4679139346$

$w_3 = w_4 = 0.3607615730$

$w_5 = w_6 = 0.1713244924$

$\xi_1 = 0.2386191861$

$\xi_2 = -0.2386191861$

$\xi_3 = 0.6612093865$

$\xi_4 = -0.6612093865$

$\xi_5 = 0.9324695142$

$\xi_6 = -0.9324695142$

The value of X_i and Z_i are calculated according to

$X_i = X_T(1+\xi_i)/2.$

$$Z_i = Z_T(1+\xi_i)/2.$$

where X_T is the total conversion at the end of the reactor and Z_T is the total length of the reactor. Therefore integral I which is a function of K_o, E, and Z evaluated at Z_1 becomes $F_1(K_o,E)$. Similarly the rest of the five functions become $F_2(K_o,E)$, $F_3(K_o,E)$, $F_4(K_o,E)$, $F_5(K_o,E)$, and $F_6(K_o,E)$. The value of the integral I is given as follows:

$$I = \frac{Z_T}{2}\,(w_1F_1(K_o,E) + w_2F_2(K_o,E) + w_3F_3(K_o,E) + w_4F_4(K_o,E) + w_5F_5(K_o,E) + w_6F_6(K_o,E)) \quad (5)$$

where:

$F_i(K_o,E) = K_o \exp(E/RT_o(1-T_o/T(Z_i)))$,

w_i = Gauss Quadrature constants.

The reaction temperature which was measured inside the reactor as a function of Z was found by curve fitting the axial temperature profile by a fourth order polynomial:

$$T = a_o + a_1Z + a_2Z^2 + a_3Z^3 + a_4Z^4. \quad (6)$$

The coefficients (a_o, a_1, a_2, a_3, and a_4) for the reaction temperature profile of all reactions inside the reactor are listed in Appendix C.

The nonlinear regression program from the "Statistical Analysis System" (SAS) package was applied to determine the parameters (m, n, K_o, and E). The nonlinear regression was performed in two stages. First, all four parameters, K_o, E, m, and n were evaluated. Thus a set of values of C_{oxy} were given and $F_i(K_o,E)$ was generated from integral I. A nonlinear regression analysis was performed with these data and the parameters K_o, E, m, and n were evaluated. For the second stage, the m and n evaluated from first stage were applied in equation (4) and only K_o and E were evaluated by nonlinear regression. Since m was equal to one, $-\ln(1 - X_{oxy})$ was used on the left hand side of equation (4), and K_o and E were evaluated by nonlinear regression. The computer program that was used for the nonlinear regression is shown in Appendix D.

The parameters for the oxygen removal of the pine pyrolytic oil with different catalysts are listed in Table 7.

Table 7. Parameters for oxygen removal model

	m	n	$K_o^*(cm^{-1} \cdot kPa^{-n})$	E (kJ/gmole)
Pt/Al_2O_3	1.0	1.0	$1.50 \pm 0.02 * 10^{-7}$	45.5 ± 3.2
CoMo	1.0	0.3	$1.07 \pm 0.07 * 10^{-3}$	71.4 ± 14.6
NiMo	1.0	0.5	$7.00 \pm 0.22 * 10^{-5}$	61.7 ± 7.1

* K_o : evaluated at 648 K (375°C).

No data using Pt/Al_2O_3 catalyst for hydrodeoxygenation (HDO) has been reported in the literature. The Pt catalyst exhibits the best activity for oxygen removal for pine pyrolytic oil among the four catalysts tested.

Although the experimental data shows the changes in space velocity did not affect oxygen removal, the "activation energies" developed from this oxygen removal model for CoMo and NiMo catalysts agree with those reported on literature. The "activation energy" for HDO using CoMo catalyst agrees with the activation energy (84.4 kJ/gmole) for HDO of a naphtha fraction obtained from coal liquid (Ternan and Brown, 1982). No H_2 pressure effect on HDO using CoMo catalyst has been reported.

The "activation energy" for HDO using NiMo catalyst is 61.7 ± 7.1 kJ/gmole. This value agrees with the activation energy for HDO of Dibenzofuran using NiMo catalyst (Krishnamurthy et al., 1981):

$$\text{Dibenzofuran} \longrightarrow \text{Biphenyl}, \quad E = 68.4 \text{ kJ/gmole;}$$

$$\text{Dibenzofuran} \longrightarrow \text{Cyclohexylbenzene}, \quad E = 76.2 \text{ kJ/gmole.}$$

Although the Pt/Al_2O_3 catalyst exhibits the best HDO ability for pine pyrolytic oil among the four catalysts tested, only 55% oxygen in pine pyrolytic oil were removed. As shown later in this chapter, the hydrotreated oil products still contain a certain amount of phenols. In order to remove more oxygen, a higher reaction temperature and pressure should be applied.

Upgrading Pine Pyrolytic Oil

Although pine pyrolytic oil and its hydrotreated products are extremely complex and are composed of hundreds of compounds, a separation method can be based on the concept of SEC separation of pyrolytic oil into fractions which are composed of only the following type of chemical groups: nonvolatiles, alkanes, phenols, and aromatics. Gas chromatography (GC) with the use of an internal standard (1-decene) gives percentage of volatiles. The nonvolatiles are soluble in THF but they cannot be detected by GC.

Figure 1 in Chapter 1 illustrates the GC-MS profile of pine pyrolytic oil before the SEC separation and the major peaks are identified and listed in Table 3. Although a number of components are identified by the GC-MS, a number of species of interest are not identified due to: (a) their low concentration levels below the MS detection levels, and (b) the overlapping of certain species such as aromatics by phenols which are major constituents with excessive peak tailing. GC-MS fails to detect a large number of aromatics. The separation of aromatics from the bulk of the oil can solve both problems and facilitate the detection and identification of aromatics by GC-MS.

The pine pyrolytic oil sample separated by SEC was divided into four fractions (Figure 9). The liquid collected in SEC fraction 1 was a black solution. As retension volume increased, the color of the SEC elutes eventually turning to a light yellow in SEC fraction 4. The average weight percentage of each fraction (after removing

THF) is listed in Table 8. Also listed in Table 8 are the volatiles, which are the total amount of components separated by the SP-2100 column and estimated by using 1-decene as an internal standard.

Table 8. Average weight percentage of SEC fractions and its volatiles of pine pyrolytic oil

FRACTION NUMBER	AVERAGE WEIGHT % (SEC)	% VOLATILES IN FRACTION (GC)	% NONVOLATILES IN FRACTION	% VOLATILES IN SAMPLE
1	11.10	0.0	100.0	0.0
2	38.12	2.67	97.33	1.04
3	42.82	28.76	71.24	12.32
4	7.86	18.60	81.40	1.46
	99.90			14.82

The SEC fraction 1 of pine pyrolytic oil is composed of high molecular-weight species. The GC analysis with the oven temperature programmed to 300°C did not detect any volatiles. Alkanes, mostly straight-chain hydrocarbons should be the volatile species expected in fraction 2. Figure 10 shows that long-chain esters are present instead of alkanes. The long-chain esters were identified by GC-MS. The low percentage of volatiles (2.67%) in Table 8 shows that most compounds in fraction 2 are nonvolatiles.

All the phenols are expected to appear in fraction 3. Large

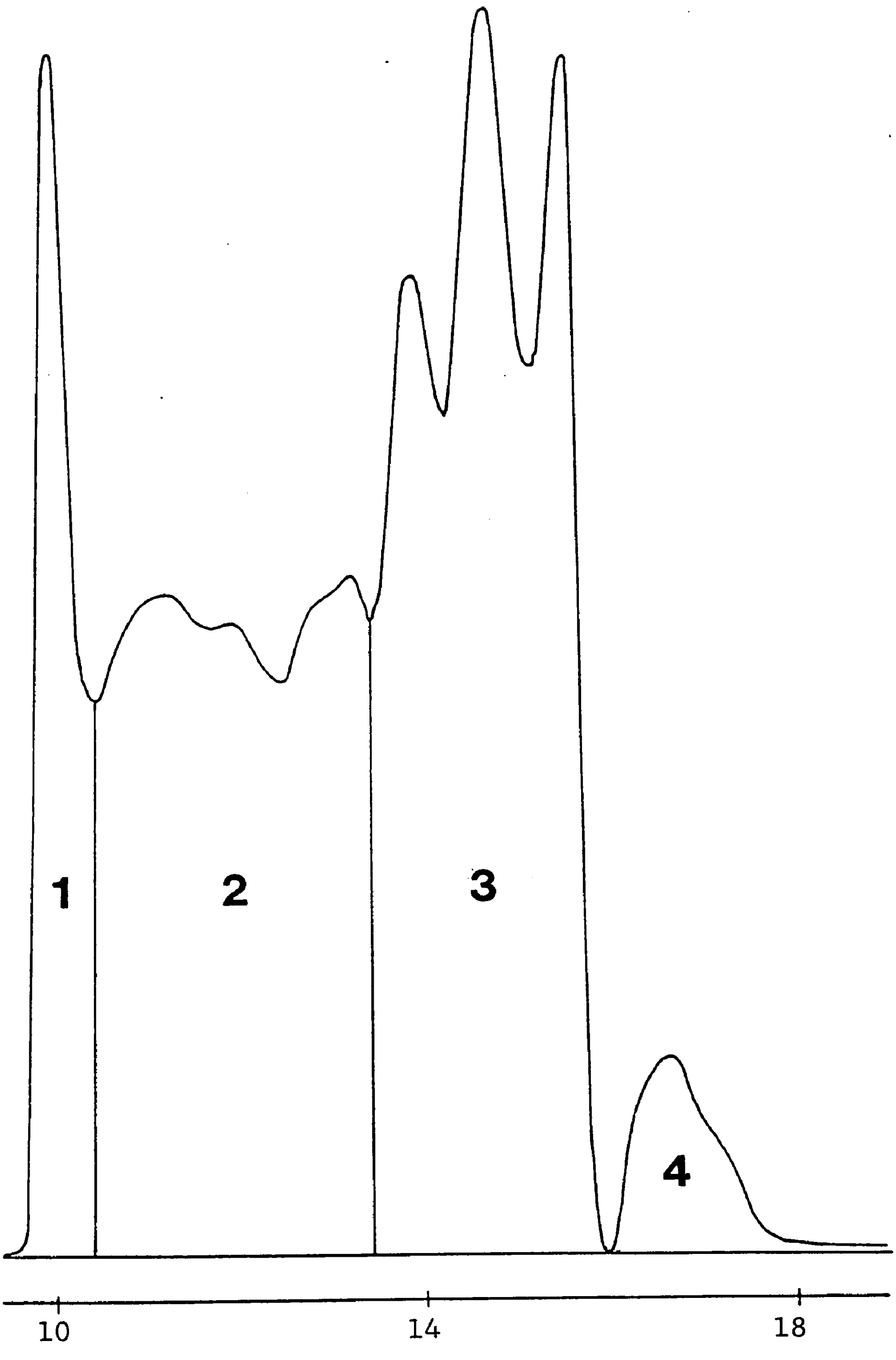

Figure 9. SEC of pine pyrolytic oil. Fractions: (1) nonvolatiles + colloidal carbons, (2) esters + nonvolatiles, (3) phenols, (4) aromatics.

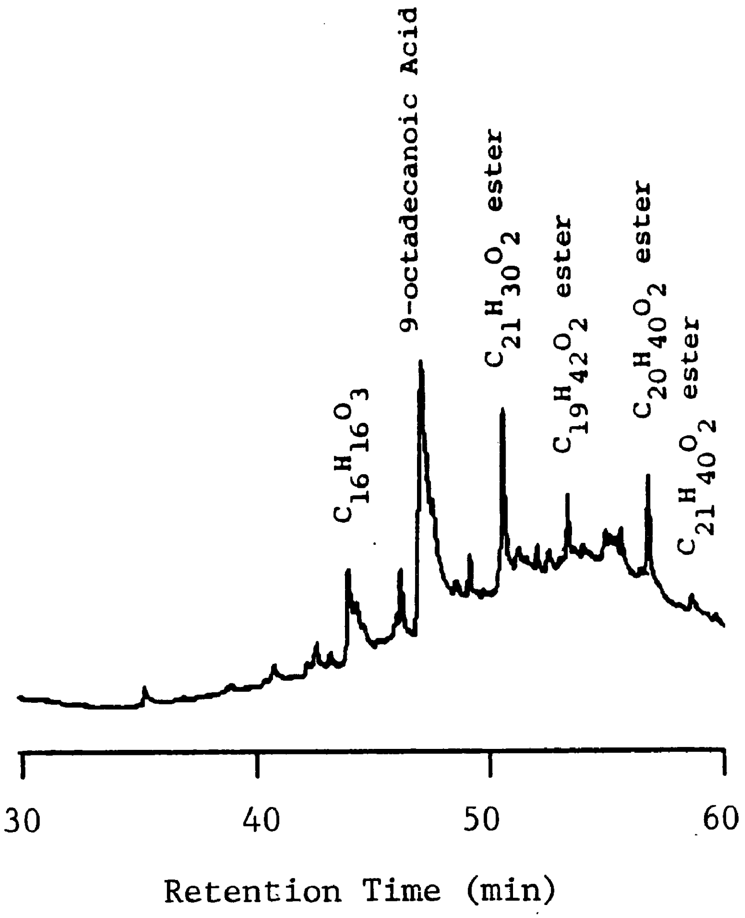

Figure 10. GC of SEC fraction 2 of pine pyrolytic oil. GC conditions: DB-5 fused silica capillary column, on-column injection, carrier gas: He, 5ml/min, temperature program, 30 to 100°C at 3°C/min, 100 to 280°C at 6°C/min.

aromatics and smaller nonvolatiles could also be present in this fraction. The GC of fraction 3 is shown in Figure 11 and the major peaks are identified by GC-MS. As expected, the volatile species in this fraction are phenols. The proportion of volatiles for this fraction is only about 30%. One reason for the low volatiles content is that water is present in pine pyrolytic oil at about 10% by weight, and water has the same retention volume as heptane which gives a negative peak in the SEC. Part of the water was collected in the phenolic fraction. The rest of the water was in the aromatic fraction.

The species in fraction 4 have linear molecular sizes smaller than that of heptane and aromatics and similiar molecular size species are expected in this fraction. Figure 12 shows the GC-MS profile. The peaks are identified by matching with reference spectra and are listed in Table 9. The fraction contains the oxygenated species which do not readily hydrogen bond with THF. These species as noted in Table 9 are principally the aldehydes, ketones, and ethers. The major loss in this fraction is water which can not be detected by the FID detector. A comparison of the components listed in Table 1 and Table 9 shows that trace aromatic components in pine pyrolytic oil which contains substantial amounts of phenols could not be identified by GC-MS prior to the separation of the sample by SEC because the phenols have broader peaks and can mask trace aromatics.

The SEC of hydrotreated pyrolytic oil (Reaction No.: 220) mixed with the processed solvent (decalin, tetralin, and naphthalene) is

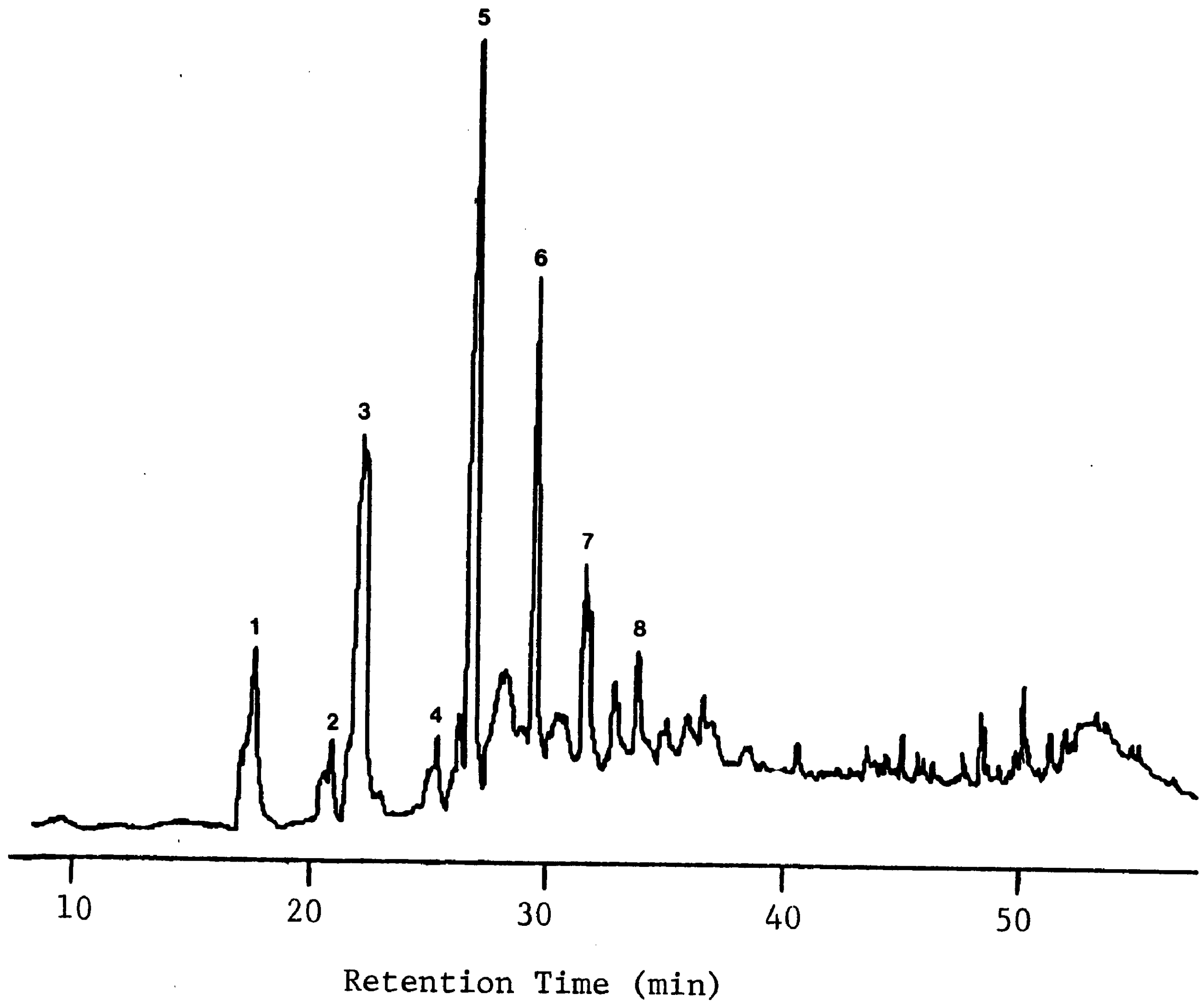

Figure 11. GC of SEC fraction 3 (phenols) of pine pyrolytic oil. Column and flow conditions as in Figure 10. Numbers correspond to peaks: (1) phenol, (2) m,p-cresol, (3) guaiacol, (4) dimethyl phenol, (5) 4-methyl guaiacol, (6) 4-ethyl guaiacol, (7) eugenol, (8) isoeugenol.

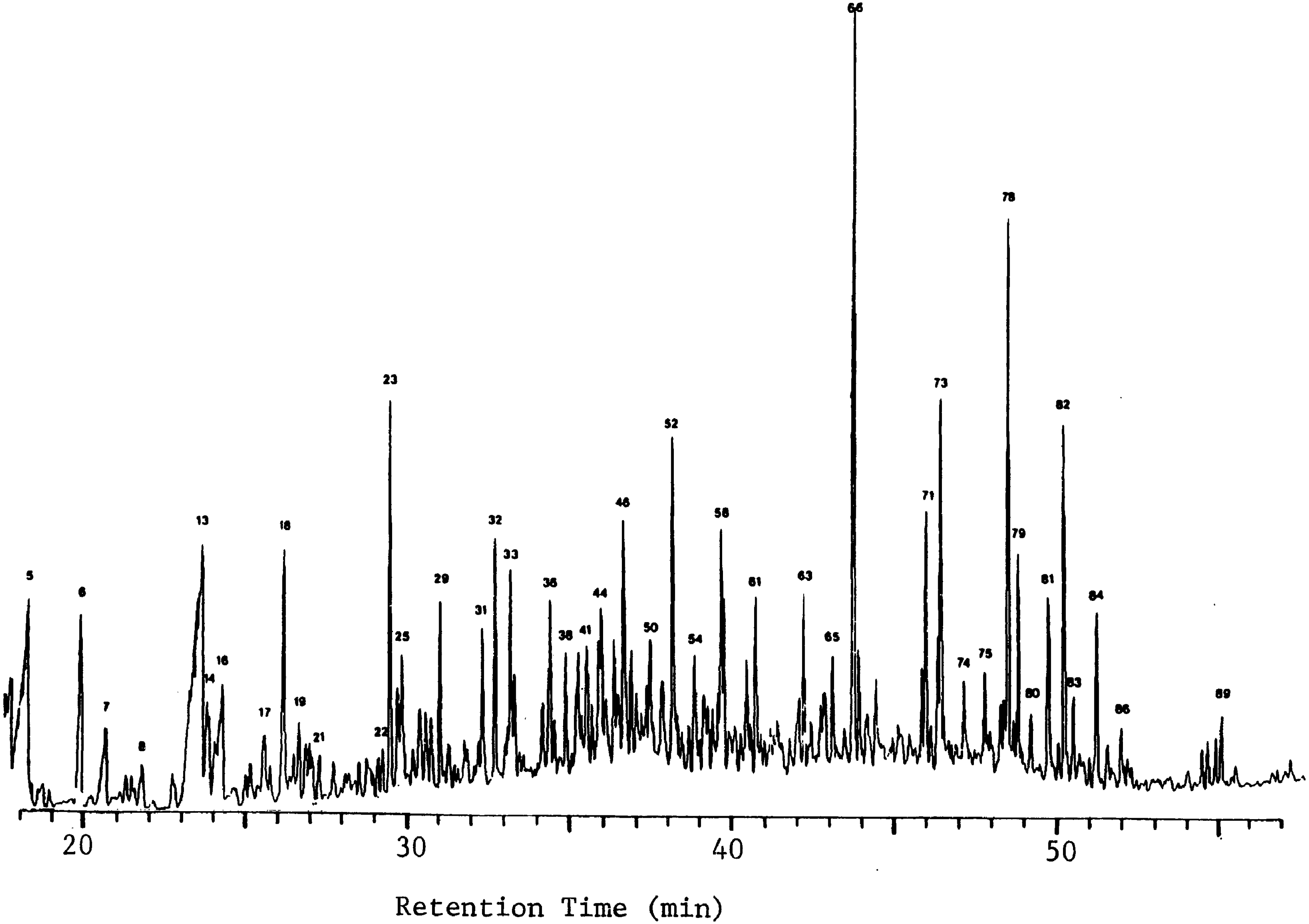

Figure 12. GC of SEC fraction 4 (aromatics) in pine pyrolytic oil. Column and flow conditions as in Figure 1. For identification of peaks see Table 9.

Table 9. Identified compounds in the aromatic fraction of pine pyrolytic oil (SEC fraction 4)

PEAK NUMBER	RETENTION TIME	COMPOUND NAME
1	8.48	Toluene
2	11.67	2-Furancarboxaldehyde
3	15.70	2-Methyl-2-cyclopenten-1-one
4	16.12	1-(2-Furanyl)-ethanone
5	17.25	$C_7H_{14}O$
6	18.93	Methylfuraldehyde
7	19.62	3-mFuranone
8	20.83	Dimethylfuranone
9	22.22	2-Hydroxy-3-methyl-2-cyclopenten-1-one
10	22.30	2-Hydroxy-3-methyl-2-cyclopenten-1-one
11	22.50	2-Hydroxy-3-methyl-2-cyclopenten-1-one
12	22.55	2-Hydroxy-3-methyl-2-cyclopenten-1-one
13	22.68	2-Hydroxy-3-methyl-2-cyclopenten-1-one
14	22.80	3-Isopropylcyclopentene
15	23.08	$C_7H_{16}O$
16	23.33	$C_7H_{16}O$
17	24.65	1-Ethylcyclohexene
18	25.25	4-Methoxyphenol
19	25.72	5-Methylbenzofuran
20	25.93	2-Ethylbenzofuran
21	26.35	Cyclohexylethanone
22	28.33	$C_8H_{14}O$
23	28.58	Naphthalene
25	28.93	$C_8H_{16}O_2$
26	29.50	4,7-Dimethylbenzofuran
27	29.68	$C_{10}H_{10}O_2$
30	30.88	2-Methyl-3(2H)-benzofuran
31	31.43	2,3-Dihydro-1H-inden-1-one
32	31.83	1-Methylnaphthalene
33	32.32	2-Methylnaphthalene
36	33.53	C_6-Alkylbenzene
37	33.68	C_6-Alkylbenzene
38	34.02	1,2-Dihydro-acenaphthalene

Table 9 (continued)

PEAK NUMBER	RETENTION TIME	COMPOUND NAME
43	35.05	Dimethylnaphthalene
44	35.13	Dimethylnaphthalene
45	35.53	Dimethylnaphthalene
46	35.83	Acenaphthalene
47	36.07	Tetrahydro-dimethylnaphthalenone
48	36.22	Tetrahydro-dimethylnaphthalenone
50	36.65	Acenaphthene
52	37.35	Dibenzofuran
53	37.83	$C_{12}H_8O$
57	38.75	C_4-Alkylnaphthalene
58	38.85	9H-Fluorene
59	38.93	2-(1-Methylethyl)-naphthalene
61	39.92	1-Methyldibenzofuran
62	41.27	2-Methyldibenzofuran
64	41.93	1-Methoxyfluorene
65	42.32	2-Methoxyfluorene
66	42.98	Phenanthrene
67	43.13	Anthracene
70	45.08	Methylphenanthrene
71	45.22	Methylphenanthrene
72	45.57	Methylphenanthrene
73	45.67	Methylphenanthrene
74	46.38	2-Phenylnaphthalene
75	47.03	Ethylphenanthrene
76	47.55	Ethylphenanthrene
77	47.63	Dimethylphenanthrene
78	47.78	Dimethylphenanthrene
79	48.10	Fluoranthene
80	48.50	Pyrene
81	49.03	Methylpyrene
82	49.53	Isopropylphenanthrene
83	49.82	Isopropylphenanthrene
84	50.52	C_4-Alkylphenanthrene
85	50.87	Trimethylphenanthrene
86	51.28	C_4-Alkylphenanthrene
88	54.20	Triphenylene
89	54.37	Chrysene

shown in Figure 13. The sample was separated into five fractions. Table 10 lists average weight percentage and volatiles of the hydrotreated pyrolytic oil.

Table 10. Weight percentage of SEC fractions and its volatiles of hydrotreated pine pyrolytic oil. Reaction conditions: 673 K, 8720 kPa, WHSV = $2hr^{-1}$.

Fraction*	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	4.45	0.0	4.45
2	23.38	3.27	20.12
3	28.95	10.63	18.32
4**	27.35	16.25	11.10
Total	84.13	30.15	53.98

* Excluding solvents (decalin, tetralin, and naphthalene).

** Including the aromatics shown in fraction 5 (solvent fraction).

By comparing the SEC of pine pyrolytic oil (Figure 9) and its hydrotreated product (Figure 13), we see the major difference is the absence of high molecular weight species (nonvolatiles) which account for the SEC area corresponding to fractions 1 and 2. Alkanes are the only volatile compounds expected to be present in fraction 2. The other species which form the bulk of this fraction are nonvolatiles.

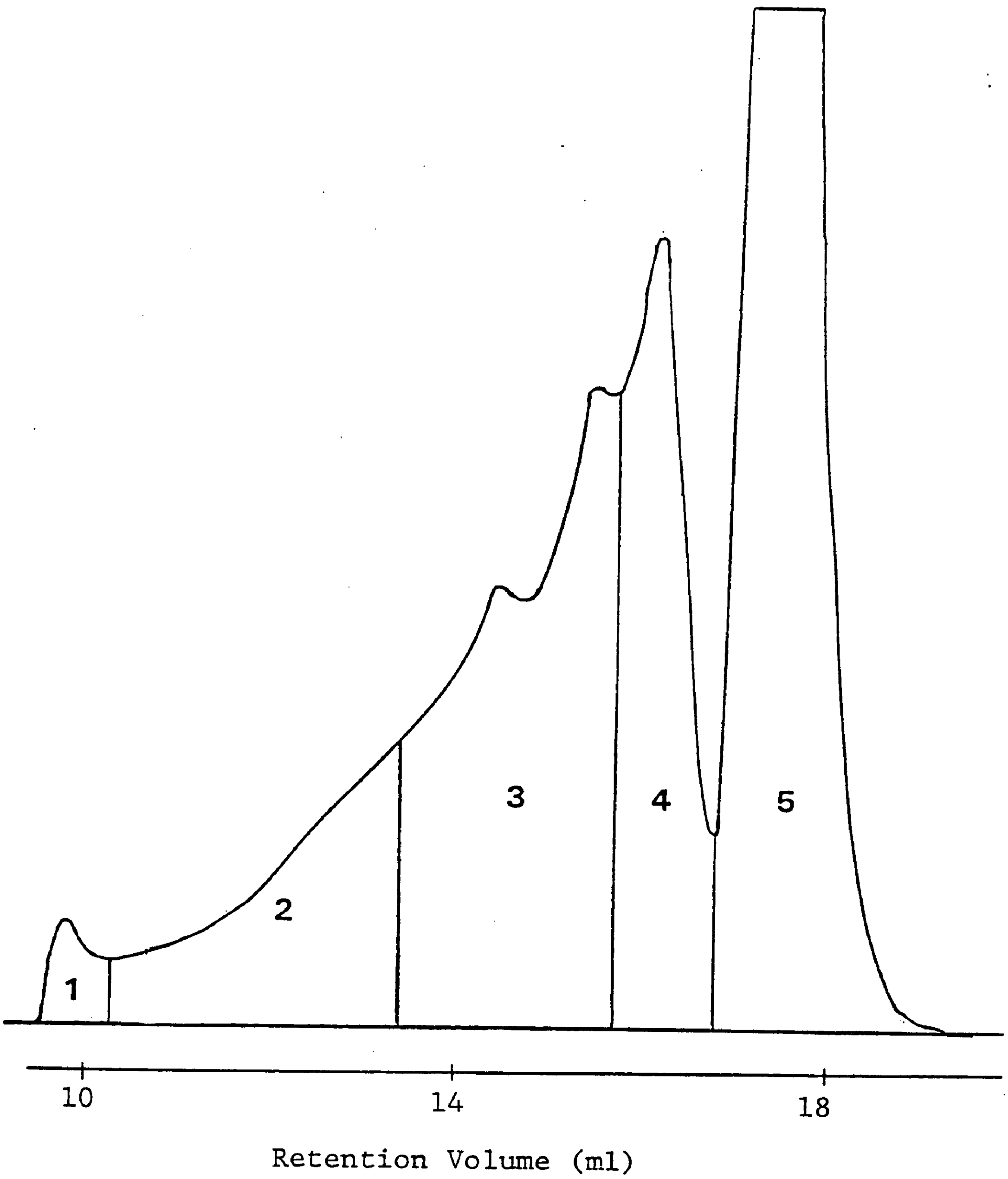

Figure 13. SEC of hydrotreated pyrolytic oil (Reaction No.: 220). Fractions: (1) nonvolatiles + colloidal carbons, (2) alkanes + nonvolatiles, (3) phenols, (4) aromatics, and (5) solvents + aromatics.

Again, the amount of the alkanes can be determined by GC. The GC of fraction 2 that is shown in Figure 14 indicates that the volatile compounds in this fraction are alkanes. The esters, which are the predominant species in the SEC fraction 2 of pine pyrolytic oil are absent. During the upgrading process using catalytic reductive hydrogenation, oxygen atoms were removed from the esters to produce alkanes. In the SEC separation, as retention volume increased, the color of the SEC elutes changed from black in fraction 1 to light yellow in fraction 5.

The SEC in Figure 13 shows that the phenolic fraction (fraction 3) of the hydrotreated oil is smaller compared to the phenolic fraction (Figure 9) of the oil before upgrading. During the upgrading process, it appears that some of the phenols are deoxygenated to aromatics. The GC outputs of fractions 3 and 4 of hydrotreated oil are shown in Figures 15 and 16, respectively. As shown in Figure 17, fraction 5 is composed of species of linear molecular size smaller than that of n-butane. The GC-MS analysis of the fraction confirmed that the solvent, decalin, tetralin, and naphthalene are the dominant eluents in this fraction.

Lumped Kinetic Modelling

Because many species are contained in pine pyrolytic oil and its hydrotreated products, the lumping together of series of constituents with similar functional groups is a useful approach. Lumped kinetic models provide a means of quantifying the effects of process variables on product yields and also of summarizing large amounts of

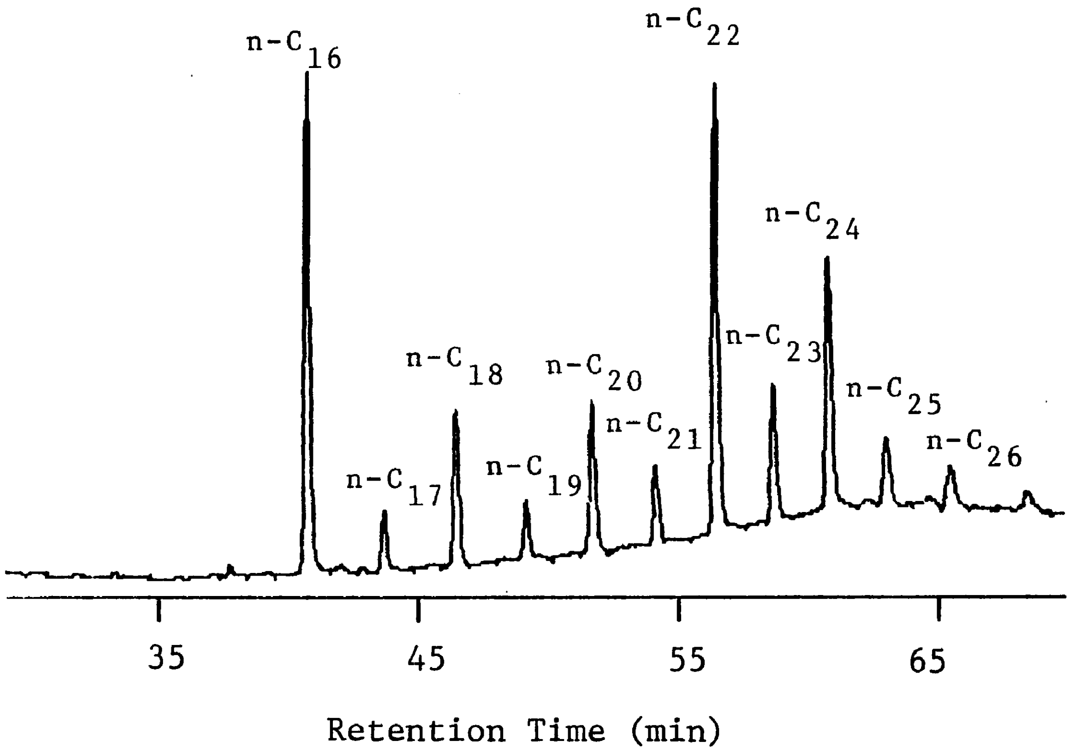

Figure 14. GC of SEC fraction 2 (alkanes) of hydrotreated pyrolytic oil (Reaction No.: 220). Conditions: SP-2100 column, carrier gas He: 40 ml/min, temperature program: 50 to 280°C at 4°C/min, initial hold 3 min.

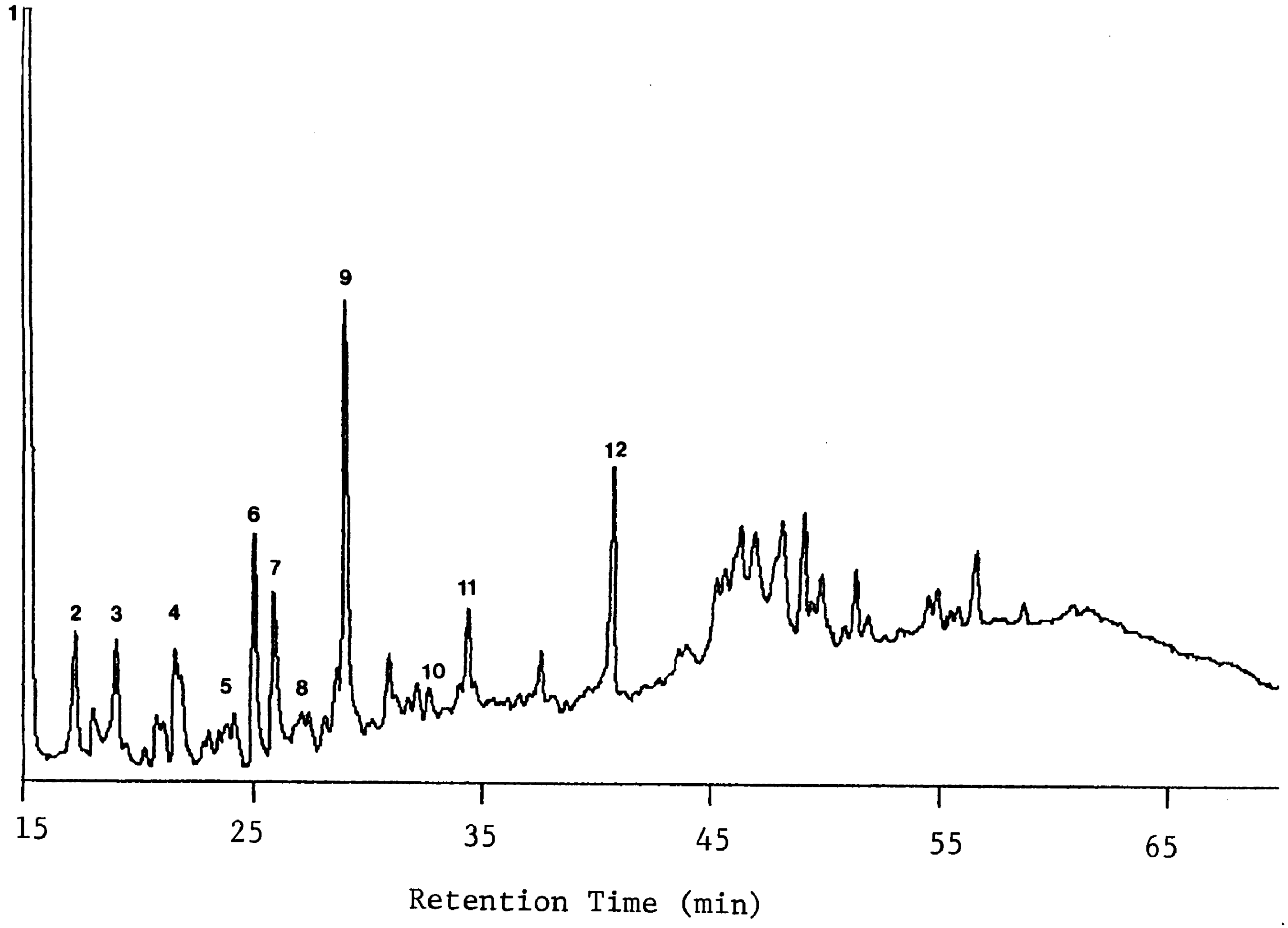

Figure 15. GC of SEC fraction 3 (phenols) of hydrotreated oil (Reaction No.: 220). Column and flow conditions as in Figure 14. Numbers correspond to peaks: (1) 1-decene (ISD), (2) o-cresol, (3) m,p-cresol, (4) and (5) C_2-phenol, (6) and (7) C_3-phenol, (8) 2-phenyl phenol, (9) C_4-phenol, (10) naphthol, (11) C_5-phenol, (12) C_6-phenol.

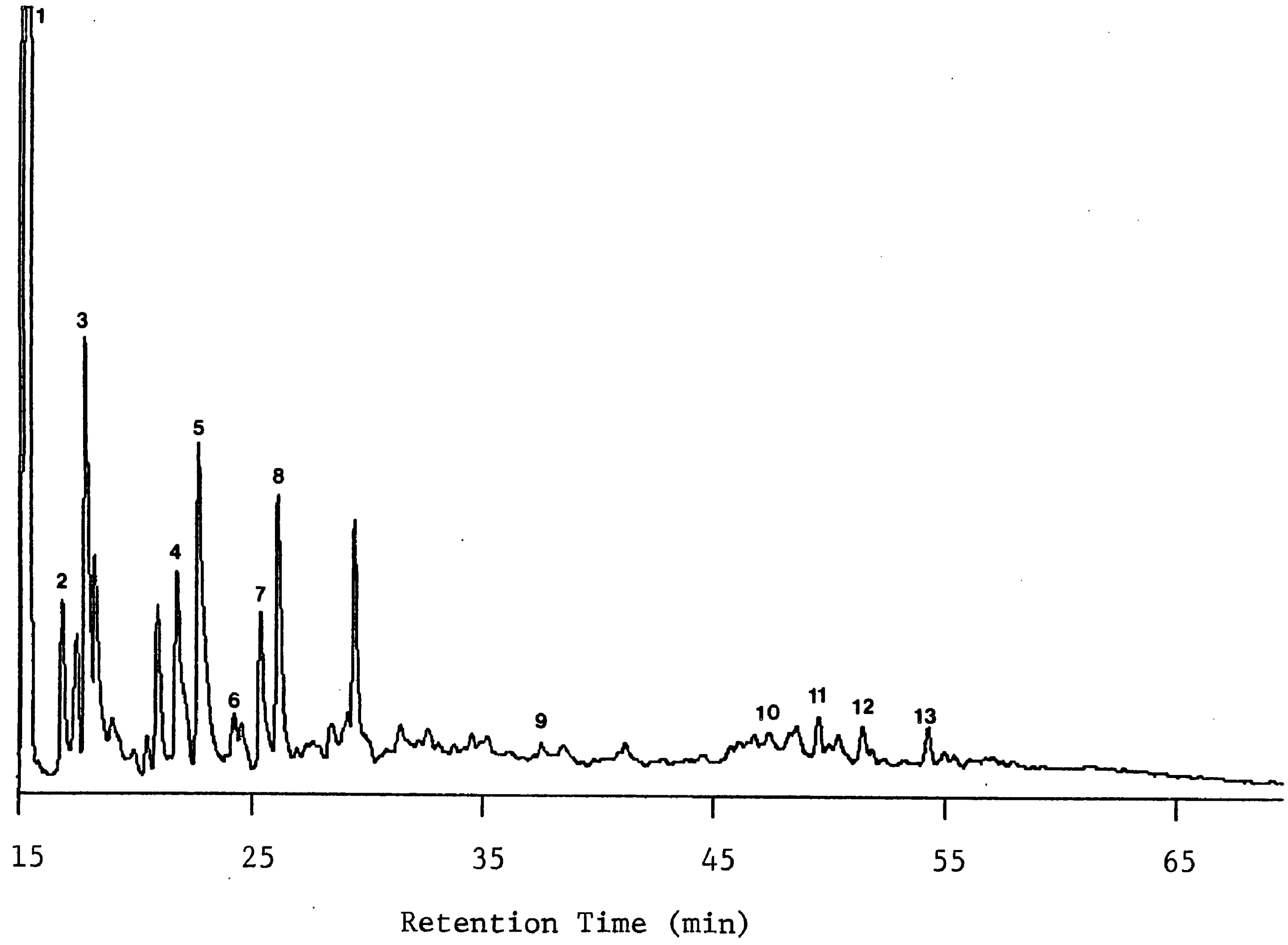

Figure 16. GC of SEC fraction 4 (aromatics) of hydrotreated pyrolytic oil (Reaction No.: 220). Column and flow conditions as in Figure 14. Numbers correspond to peaks: (1) 1-decene (STD) (2) butylcyclohexane (3) butylbenzene (4) C_5-cyclohexane (5) C_5-benzene (6) dimethylindane (7) methyltetralin (8) methylcyclohexyl cyclohexane (9) dimethylbiphenyl (10) phenanthrene (11) C_1-phenanthrene (12) C_2-phenanthrene (13) C_3-phenanthrene.

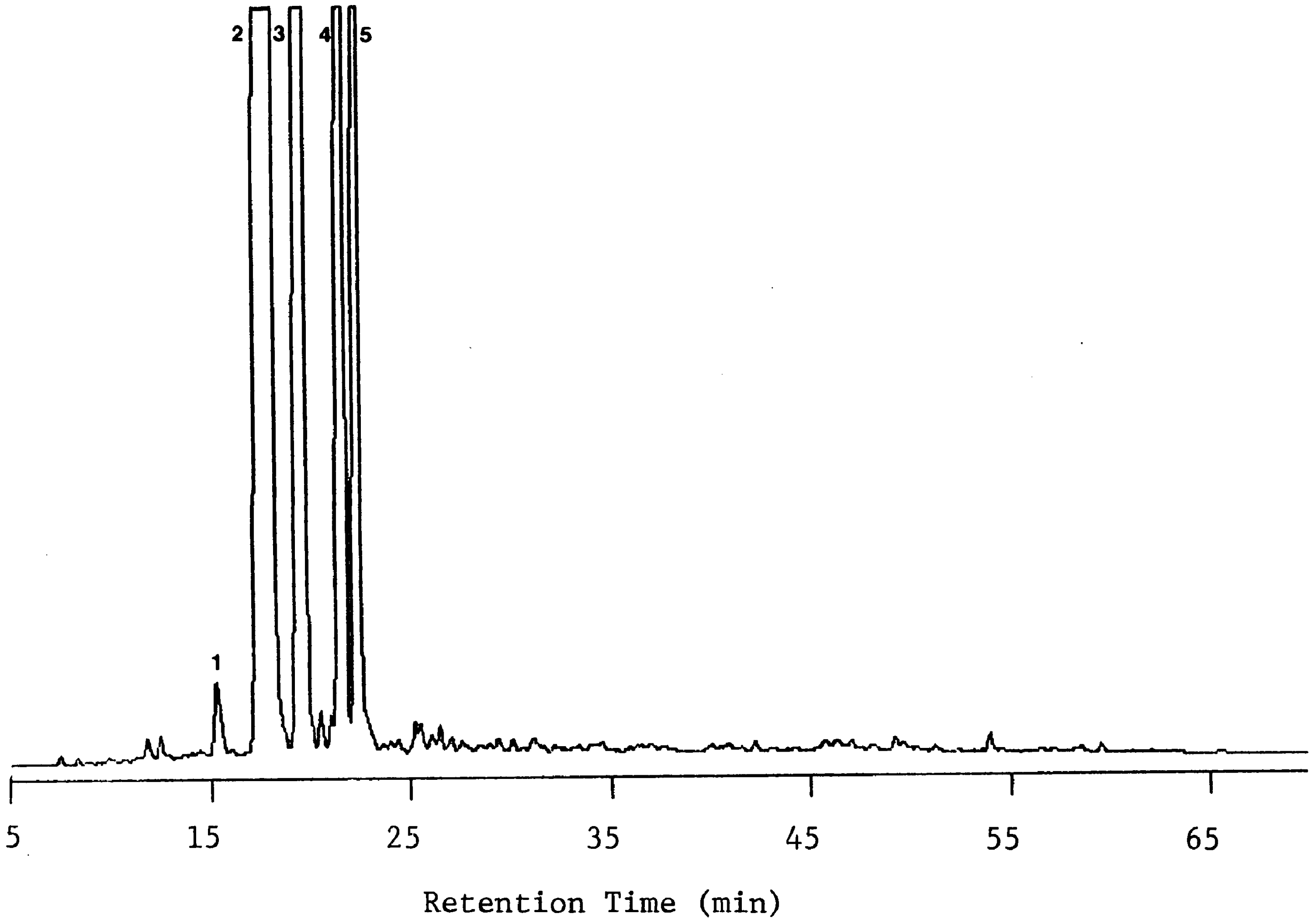

Figure 17. GC of SEC fraction 5 (solvents + aromatics) of hydrotreated pyrolytic oil (Reaction No.: 220). Column and flow conditions as in Figure 14. Numbers correspond to peaks: (1) 1-decene (STD) (2) trans-decalin (3) cis-decalin (4) tetralin (5) naphthalene.

experimental data.

Data obtained from the SEC-GC analysis were modeled with pseudo first order kinetics describing the reaction rates of lumped species. An Arrhenius model was used to describe the temperature dependence of the rate constants. The proposed kinetic model for hydrotreating pyrolytic oil consists of the kinetic scheme is shown in Figure 18. The terms used in Figure 18 are defined as follows:

Heavy nonvolatiles = nonvolatiles in SEC fraction 1
+ nonvolatiles in SEC fraction 2.

Light nonvolatiles = nonvolatiles in SEC fraction 3
+ nonvolatiles in SEC fraction 4.

Phenols = volatiles in SEC fraction 3
(compounds detectable by GC).

Aromatics = volatiles in SEC fraction 4
+ volatiles in fraction 5
(excluding solvents).

Alkanes = volatiles in SEC fraction 2

Coke + H_2O + Outlet Gases = 1 - liquid yield of hydrotreated reaction.

The liquid yield of hydrotreatment is defined as follows:

$$\text{Liquid Yield} = \frac{\Sigma(\text{wt. of fractions by SEC}) - (\text{solvents in hydrotreated oil})}{\text{pine pyrolytic oil input}}$$

The Σ(wt. of fractions by SEC) represents the weight of liquid product which includes the hydrotreated oil and solvents. During the hydrotreating reaction, the pine pyrolytic oil produced three different phase products: solid (coke deposited on catalyst), liquid (hydrotreated oil plus water at separated layers), and gases. The "coke + H_2O + outlet gases" represents all the pyrolytic oil products of the reaction except the hydrotreated oil. The reason for water being a product of the "aromatics + alkanes" fraction is that the SEC separation is based an linear molecular size and water contained in the pine pyrolytic oil was in the aromatics fraction before the hydrotreating reaction.

The esters in the pine pyrolytic oil was lumped into "light nonvolatiles" fraction. The "aromatics" fraction included aromatics and the species had linear molecular sizes smaller than heptane. Table 12 shows an example of the lumped fractions of the pine pyrolytic oil and a hydrotreated product (Reaction No.: 220) . All SEC–GC analytical results and lumped fraction data for kinetic modeling are listed in Appendix A.

Small trickle–bed reactors such as those used in laboratories and pilot plants have some axial despersion. The material balance for the liquid phase of the differential reactor volume increment is:

(gram inflow axially)
– (gram outflow axially)
+ (gram inflow by axial dispersion)
– (gram outflow by axial dispersion)
– (gram disappearance by reaction) = 0 (7)

Table 12. Lumped fractions for kinetic modeling

	Lumped Fraction	Pine pyrolytic oil	Hydrotreated pyrolytic oil (Reaction No.: 220)
1	Heavy Nonvolatiles:	0.4932	0.2457
2	Light Nonvolatiles:	0.3690	0.2941
3	Volatile Phenols:	0.1232	0.1063
4	Aromatics:	0.0146	0.1625
5	Alkanes:	0.0	0.0327
6	Gases + H_2O + Coke:	0.0	0.1587
		1.0000	1.0000

The value of each set of parentheses in general terms is:

$$\text{gram inflow axially} = \frac{\pi}{4} D_T^2 \, u_L \, \rho_i \big|_z$$

$$\text{gram outflow axially} = \frac{\pi}{4} D_T^2 \, u_L \, \rho_i \big|_{z+\Delta z}$$

$$\text{gram inflow by axial dispersion} = \frac{\pi}{4} D_T^2 \left(-D \frac{d\rho_i}{dZ}\bigg|_z\right)$$

$$\text{gram outflow by axial dispersion} = \frac{\pi}{4} D_T^2 \left(-D \frac{d\rho_i}{dZ}\bigg|_{z+\Delta z}\right)$$

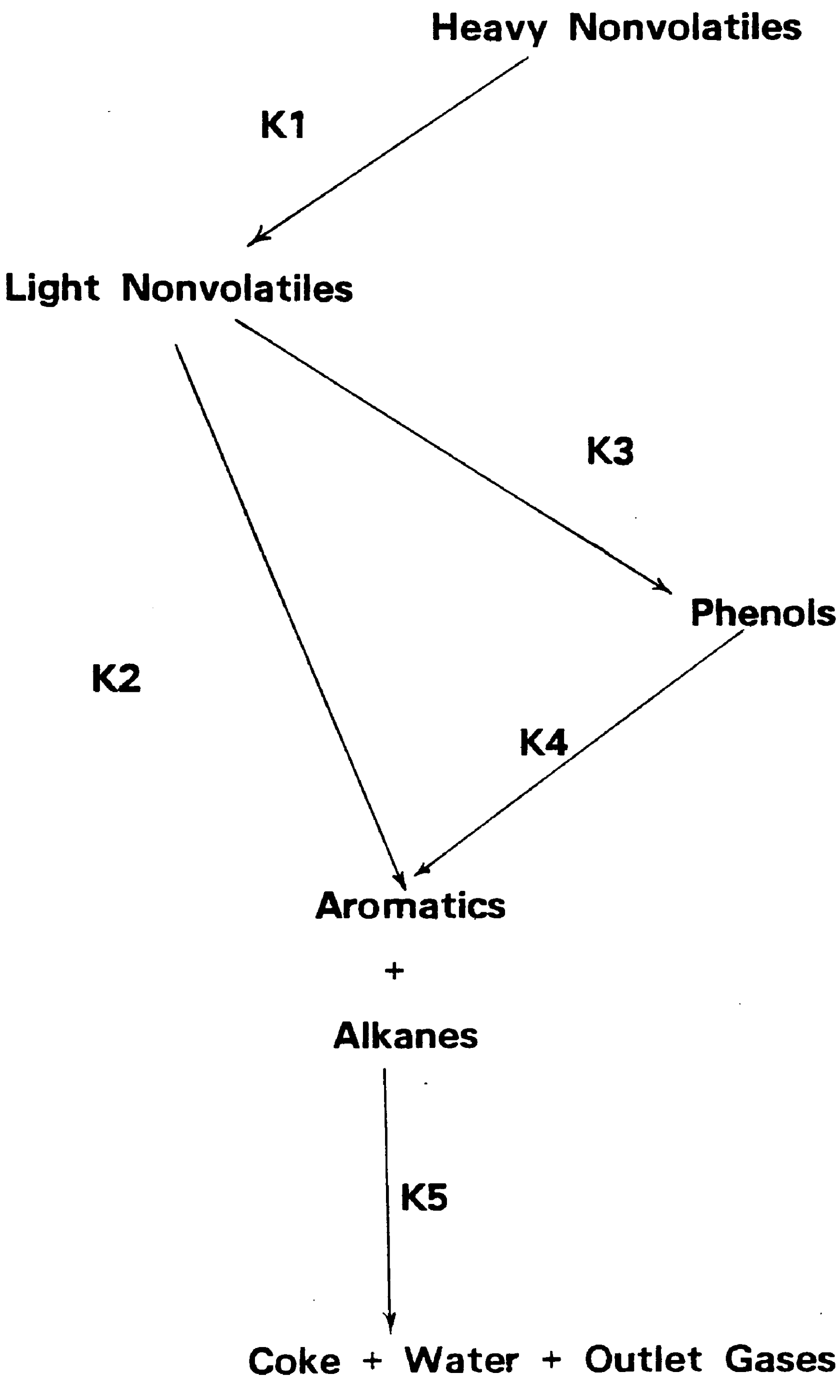

Figure 18. Lumped kinetic scheme

gram disappearence by reaction = $- \dfrac{\pi}{4} D_T^2 \, \Delta z \, \rho_B \, R_i$

where:

D = dispersion of the reacting species in liquid phase

$-D \left(\dfrac{d\rho_i}{dZ}\right)$ = the flux in axial direction according to Fick's law

D_T = reactor diameter

R_i = reaction rate of species "i"

u_L = the superficial velocity of the pyrolytic oil

z = catalytic bed legth

ρ_B = bulk catalytic bed density

ρ_i = density of reacting species "i".

Using these expressions in the material balance equation (7) and dividing both sides of the resulting equation by $(\pi/4)\ D_T^2\ \Delta z\ u_L$ gives:

$$\frac{\rho_i|_{z+\Delta z} - \rho_i|_z}{\Delta z} = \frac{D(d\rho_i/dZ)|_{z+\Delta z} - D(d\rho_i/dZ)|_z}{\Delta z\ u_L} - \frac{R_i \rho_B}{u_L} \qquad (8)$$

When $\Delta z \longrightarrow 0$, equation (8) becomes:

$$\frac{d\rho_i}{dZ} = \frac{D}{u_L}\,\frac{d^2\rho_i}{dZ^2} - \frac{R_i\rho_B}{u_L} \qquad (9)$$

Equation (9) can be converted to a dimensionless form by substituting

$$\frac{\rho_i}{\rho_o} = Y_i \qquad \text{and} \qquad \frac{z}{L} = Z$$

where L is the total catalytic bed length and ρ_o is the pine pyrolytic oil density. Thus we obtain:

$$\frac{dY_i}{dZ} = \frac{D}{u_L L}\frac{d^2Y_i}{dZ^2} - \frac{L\,\rho_B}{u_L\rho_o} R_i \tag{10}$$

Here, the term $u_L L/D$ in equation (10) is the Peclet number (Pe_M) for axial dispersion in the liquid phase. So, equation (10) can be rearranged to:

$$\frac{d^2Y_i}{dZ^2} - Pe_M \frac{dY_i}{dZ} - Pe_M \frac{L\rho_B}{u_L\rho_o} R_i = 0 \tag{11}$$

Data obtained from the SEC-GC analysis were modeled with pseudo first order kinetics describing the reaction rates of lumped species. The proposed lumped kinetic model for hydrotreating pyrolytic oil consists of the kinetic scheme is shown in Figure 18. The rate equations corresponding to the lumped species are:

$$r_1 = -K_1\rho_1 \tag{12}$$

$$r_2 = K_1\rho_1 - K_2\rho_2 - K_3\rho_2 \tag{13}$$

$$r_3 = K_3\rho_2 - K_4\rho_3 \tag{14}$$

$$r_4 = K_2\rho_2 + K_4\rho_3 - K_5\rho_4 \tag{15}$$

$$r_5 = K_5\rho_4 \tag{16}$$

where: $r_i = R_i\ \rho_B$

and the subscript "1" = heavy nonvolatiles

"2" = light nonvolatiles

"3" = volatile phenols

"4" = aromatics + alkanes

"5" = coke + H_2O + outlet gases.

An Arrhenius model was used to describe the temperature dependence of the rate constants.

$$K_i = A_i \exp(-E_i/RT)$$

For the reaction of heavy nonvolatiles in pine pyrolytic oil, substitute rate equation (12) and K_1 into equation (11) and we get:

$$\frac{d^2Y_1}{dZ^2} - Pe_M \frac{dY_1}{dZ} + Pe_M \frac{L}{u_L}\left(\frac{\rho_1}{\rho_o}\right) A_1 \exp\left(\frac{-E_1}{RT_o}\right) \exp\left(\frac{E_1}{RT_o}\right)\left(1 - \frac{T}{T_o}\right) = 0 \qquad (17)$$

Let us define: Damkohler number $(Da_i^o) = \frac{LK_{io}}{u_L}$ (18)

$$\text{and } \gamma_i = \frac{E_i}{RT_o} \qquad (19)$$

Substitute Da_1^o and γ_1 into equation (17) to obtain:

$$\frac{d^2Y_1}{dZ^2} - Pe_M \frac{dY_1}{dZ} + Pe_M\, Da_1^o \exp\left(\gamma_1\left(1 - \frac{T_o}{T}\right)\right) Y_1 = 0 \qquad (20)$$

Similar equations can be written for the other four lumped reaction species occurring in the process.

$$\frac{d^2Y_2}{dZ^2} - Pe_M \frac{dY_2}{dZ} + Pe_M\, Da_2^\circ \exp\left(\gamma_2\left(1 - \frac{T_o}{T}\right)\right) Y_2$$

$$+ Pe_M\, Da_3^\circ \exp\left(\gamma_3\left(1 - \frac{T_o}{T}\right)\right) Y_2$$

$$= Pe_M\, Da_1^\circ \exp\left(\gamma_1\left(1 - \frac{T_o}{T}\right)\right) Y_1 \qquad (21)$$

$$\frac{d^2Y_3}{dZ^2} - Pe_M \frac{dY_3}{dZ} + Pe_M\, Da_4^\circ \exp\left(\gamma_4\left(1 - \frac{T_o}{T}\right)\right) Y_3$$

$$= Pe_M\, Da_3^\circ \exp\left(\gamma_3\left(1 - \frac{T_o}{T}\right)\right) Y_2 \qquad (22)$$

$$\frac{d^2Y_4}{dZ^2} - Pe_M \frac{dY_4}{dZ} + Pe_M\, Da_5^\circ \exp\left(\gamma_5\left(1 - \frac{T_o}{T}\right)\right) Y_4$$

$$= Pe_M\, Da_4^\circ \exp\left(\gamma_4\left(1 - \frac{T_o}{T}\right)\right) Y_3$$

$$+ Pe_M\, Da_2^\circ \exp\left(\gamma_2\left(1 - \frac{T_o}{T}\right)\right) Y_2 \qquad (23)$$

$$\frac{d^2Y_5}{dZ^2} - Pe_M \frac{dY_5}{dZ} = Pe_M\, Da_5^\circ \exp\left(\gamma_5\left(1 - \frac{T_o}{T}\right)\right) Y_4 \qquad (24)$$

The boundary conditions for equations (20) through (24) are:

$$\frac{dY_i}{dZ} = Pe_M(Y_i - Y_i^\circ) \qquad \text{at } Z = 0$$

$$\frac{dY_i}{dZ} = 0 \qquad \text{at } Z = 1 \qquad (i = 1 \text{ to } 5)$$

A method of combining quasilinearization with orthogonal collocation was applied to estimate the parameters Pe_M, Da_i^o, and γ_i in equations (20) through (24) simultaneously. The method was originally developed for modeling the liquefaction of coal in a bubble column reactor (Tarng and Anthony, 1984). It has the ability to solve a large set of nonlinear boundary value ordinary differential equations.

The parameter estimation was performed on a single run basis. Thus, for each reaction run, a set of lumped fraction data from the SEC–GC analysis plus the temperature profile inside the reactor were given. Equations (20) to (24) were solved simultaneously and the parameters Pe_M, Da_i^o, and γ_i for each run were obtained. The activation energy (E_i) and frequency factor (A_i) of the lumped kinetic model were derived from the estimated parameters Da_i^o and γ_i by equations (18) and (19). The average activation energies for different catalyst are given in Table 13 along with the average frequency factors for the various steps in the reaction network. Also listed in Table 13 is the Peclet number (Pe_M). The average frequency factors listed in Table 13 were evaluated at 8720 kPa. The pressure effect on reaction rates will be discussed later.

The experimental and predicted values of the lumped species in the kinetic model at various reaction conditions are presented in the following subsections.

Table 13. Activation energy (E_i), frequency factor (A_i) (at 8720 kPa), and Peclet number (Pe_M) of the predicted lumped kinetic model

	Pt/Al_2O_3	CoMo	NiMo
E_1 (kJ/gmole)	74.0 ± 2.9	74.5 ± 3.2	82.2 ± 2.9
E_2	91.8 ± 4.3	96.4 ± 3.4	105.8 ± 3.0
E_3	80.6 ± 2.6	81.8 ± 3.6	90.4 ± 3.0
E_4	62.3 ± 2.6	69.0 ± 2.9	68.4 ± 3.4
E_5	69.6 ± 2.8	55.8 ± 3.6	74.9 ± 2.7
A_1 (min^{-1})	3860 ± 500	3500 ± 280	8800 ± 1000
A_2	75400 ± 12000	218000 ± 8400	654000 ± 59000
A_3	8300 ± 1100	7700 ± 460	30600 ± 3600
A_4	950 ± 160	3100 ± 560	1920 ± 50
A_5	4000 ± 650	450 ± 47	16400 ± 160
Pe_M	10.2 ± 1.1	9.86 ± 0.05	9.63 ± 0.38

Effect of Temperature

The effect of the reaction temperature on hydrotreated pyrolytic oil was evaluated at 623, 648, and 673 K. All reactions were run at 8720 kPa and weight hourly space velocity equal to 2 hr^{-1}. One significant difference in the reaction products at different reaction temperature was that the liquid products at 623 K did not have a water layer separated from the hydrotreated oil. Thus, the liquid product at 623 K contained the hydrotreated pyrolytic oil, solvents, and water.

Figures 19 through 21 are the GC output for the SEC phenolic fraction in the pine pyrolytic oil and for two different reaction products using Pt/Al_2O_3 as catalyst (reaction temperature = 623 and 673 K, respectively). Significant changes in phenolic fraction can be observed. The GC output of the phenolic fraction at 623 K (Figure 20) has less volatile phenols than those in pine pyrolytic oil (Figure 19). Comparing the GC of the SEC phenolic fractions of pine pyrolyic oil with a 623 K, hydrotreated product (reaction No.: 325), the major difference is the absence of the small molecular weight phenols (guaiacol, methyl-guaiacol, etc.) which have been converted into aromatics during the hydrotreating reaction. The volatile phenols in pyrolytic oil decreased from 12.3 weight% (before reaction) to 6.9 weight%. Also shown in the SEC-GC analytical data (Appendix A) is the increased amount in aromatics fraction (1.5 to 9.87 %) and alkanes fraction (0.0 to 1.9 %). Although the quantity of the alkanes and aromatics varied with different reaction conditions, the GC output of these two fractions are similiar to those shown in Figures 14 and 16.

Figure 21 is the GC output of SEC phenolic fraction at 673 K (reaction No.: 220). The phenolic peaks identified in Figure 21 are different from those shown in the same SEC fraction of pine pyrolytic oil (Figure 19). This proves that phenols are the intermediate products during the hydrotreating reaction. Comparing the two reaction temperature products, the volatile phenols increased from 6.9 (623 K) to 10.6 wt.% (673 K). The lumped aromatics fraction also increased from 9.8 to 16.2 wt%. This suggests the following reaction scheme:

$$\begin{tikzcd} \text{Light nonvolatiles} \arrow[r, "K_3"] \arrow[rr, bend right, "K_2"'] & \text{Phenolics} \arrow[r, "K_4"] & \text{Aromatics} \end{tikzcd}$$

which means part of the phenols in pine pyrolytic oil have been hydrotreated and converted into aromatics, and phenols also have been produced from the nonvolatiles during the reaction. Some aromatics were converted from the light nonvolatile fraction. The alkanes were produced by removing the oxygen atoms from the esters in the pine pyrolytic oil during the hydrotreating reaction.

The pages 81 through 83 show the comparison of experimental and predicted concentration profiles for the various species in the

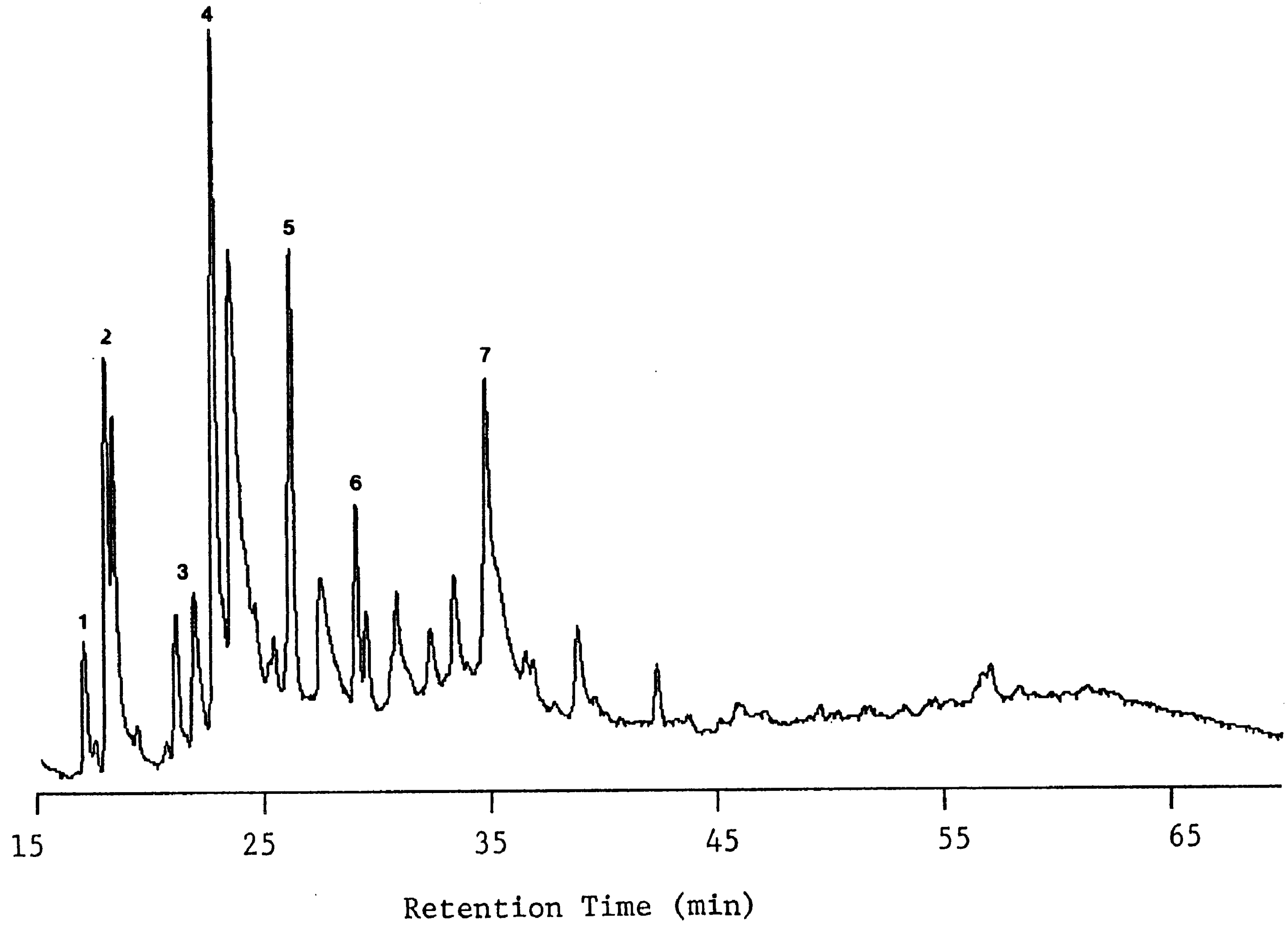

Figure 19. GC of SEC fraction 3 (phenols) of pine pyrolytic oil. Column and flow conditions as in Figure 14. Numbers correspond to peaks: (1) m,p-cresol, (2) guaiacol, (3) dimethyl phenol, (4) 4-methyl guaiacol, (5) 4-ethyl guaiacol, (6) eugenol, (7) isoeugenol.

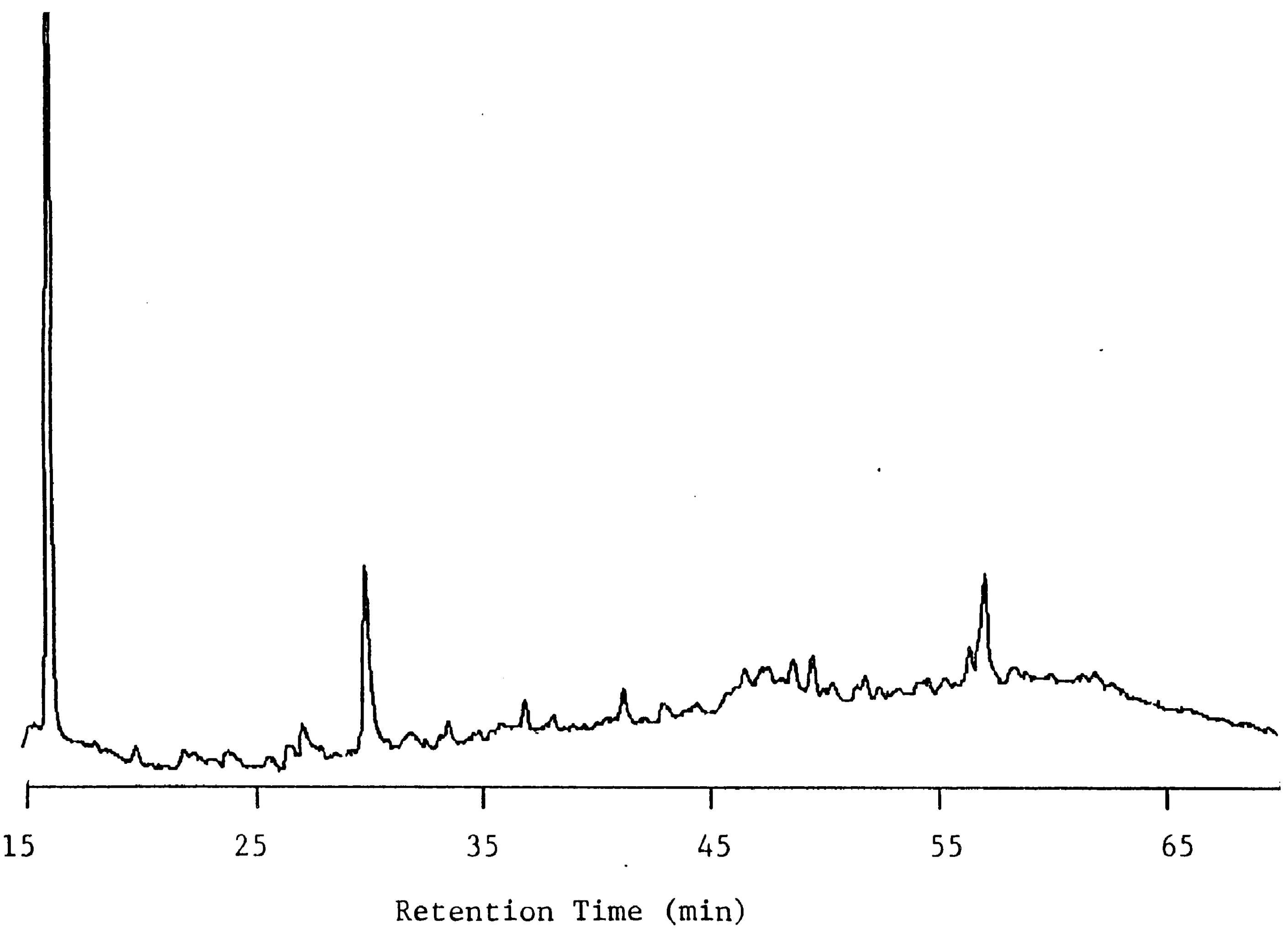

Figure 20. GC of SEC fraction 3 (phenols). Reaction conditions: Pt/Al_2O_3 catalyst, 623 K, 8720 kPa, WHSV=2 hr^{-1}. Column and flow conditons as in Figure 14.

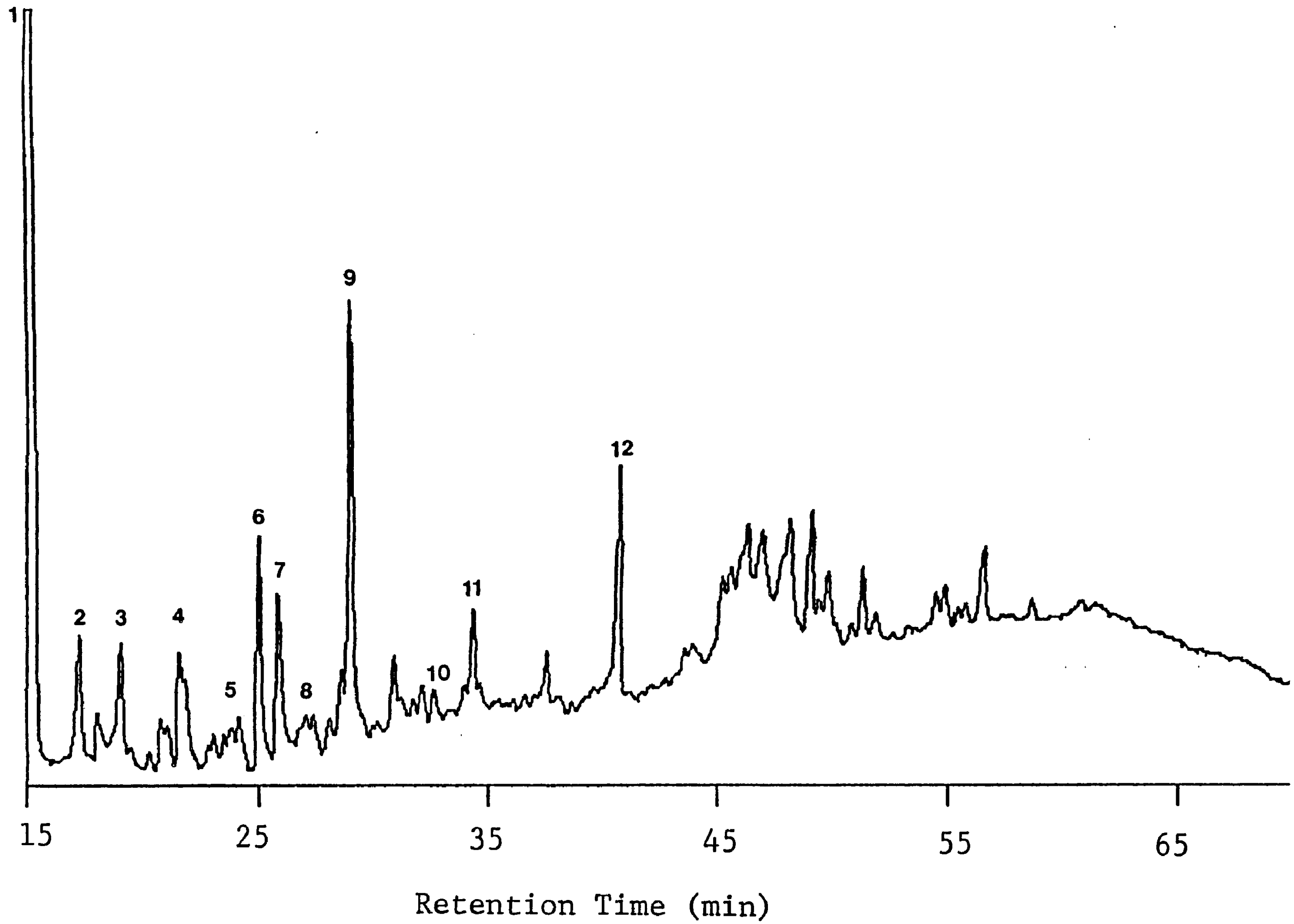

Figure 21. GC of SEC fraction 3 (phenols). Reaction conditions: Pt/Al_2O_3 catalyst, 673 K, 8720 kPa, WHSV=2 hr^{-1}. Column and flow conditons as in Figure 14. Numbers correspond to peaks: (1) 1-decene (ISD), (2) o-cresol, (3) m,p-cresol, (4) and (5) C_2-phenol, (6) and (7) C_3-phenol, (8) 2-phenyl phenol, (9) C_4-phenol, (10) naphthol, (11) C_5-phenol, (12) C_6-phenol.

lumped kinetic model. The points in the Figures are the experimental data. The solid lines were calculated from the lumped kinetic model parameters listed in Table 13. In Figures 22 and 23 (Pt/Al_2O_3 and CoMo catalysts, respectively), an 8 to 10% decrease in the "heavy nonvolatiles" and "light nonvolatiles" in the lumped model can be observed by an increase of reaction temperature from 623 to 673 K. The lumped fractions, "Phenols", "Aromatics + alkanes", and "coke + water + outlet gases", increase with higher reaction temperature. One reason for the "coke + water + outlet gases" increase with higher reaction temperature is that at 648 and 673 K reaction temperature, water in the liquid product can be separated from the hydrotreated oil.

Even though the reaction rates increased with the reaction temperature, the temperature effect on the performance of NiMo catalyst was not significant. In Figure 24, the lumped fractions only change about 1 to 4% by increasing the reaction temperature from 623 to 673 K.

Effect of Reaction Pressure

The effect of reaction pressure was evaluated at 5272, 6996, 8720, and 10443 kPa at 673 K and weight hourly space velocity equal to 2 hr^{-1}. Assume a relationship between the frequency factor in the lumped kinetic model and the reaction pressure:

$$A_i \propto P^{n_i}$$

The values of n_i were calculated and are listed in Table 14. From

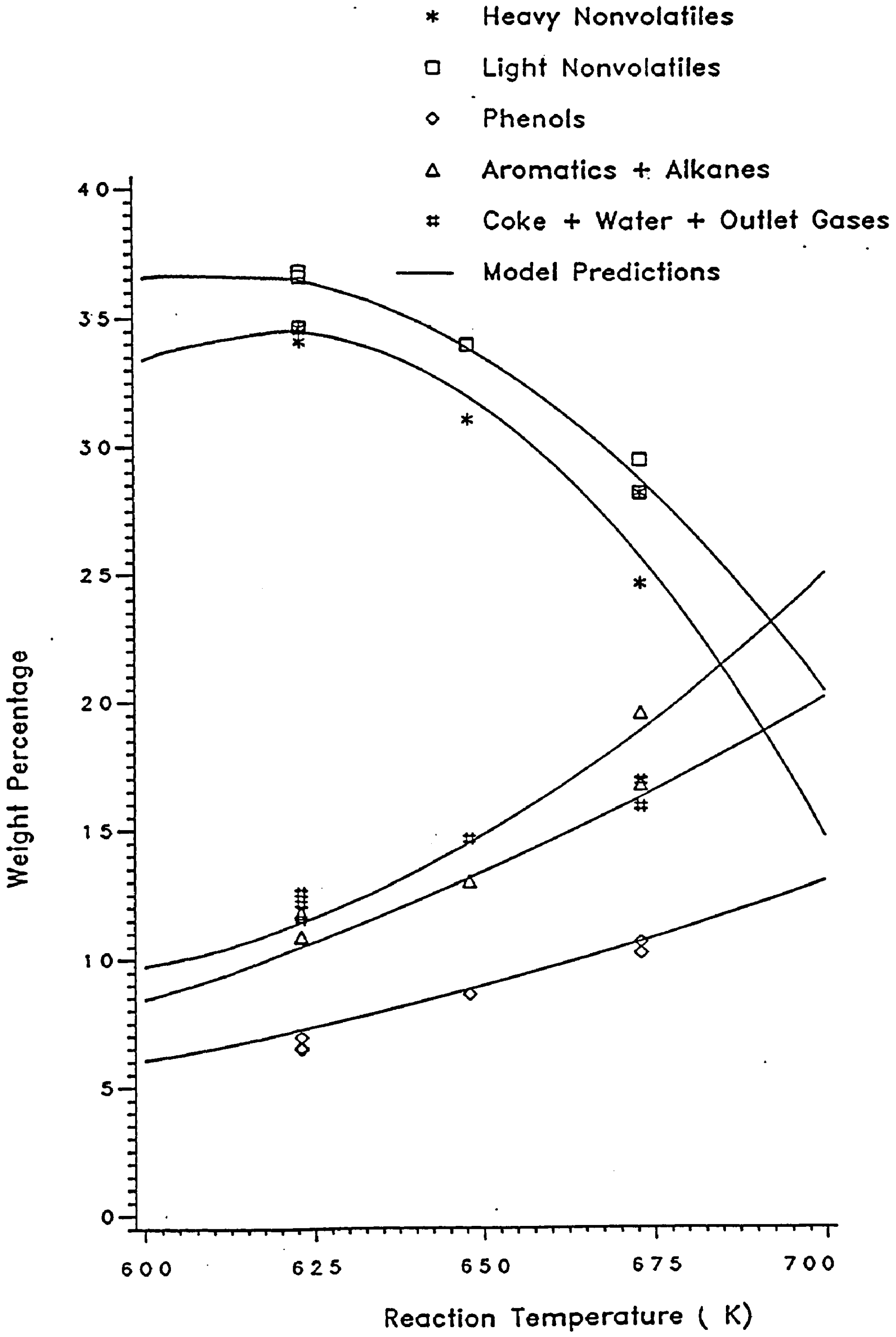

Figure 22. Temperature effect on hydrotreated pyrolytic oil product. Catalyst: Pt/Al_2O_3, pressure: 8,720 kPa, WHSV: 2 hr^{-1}.

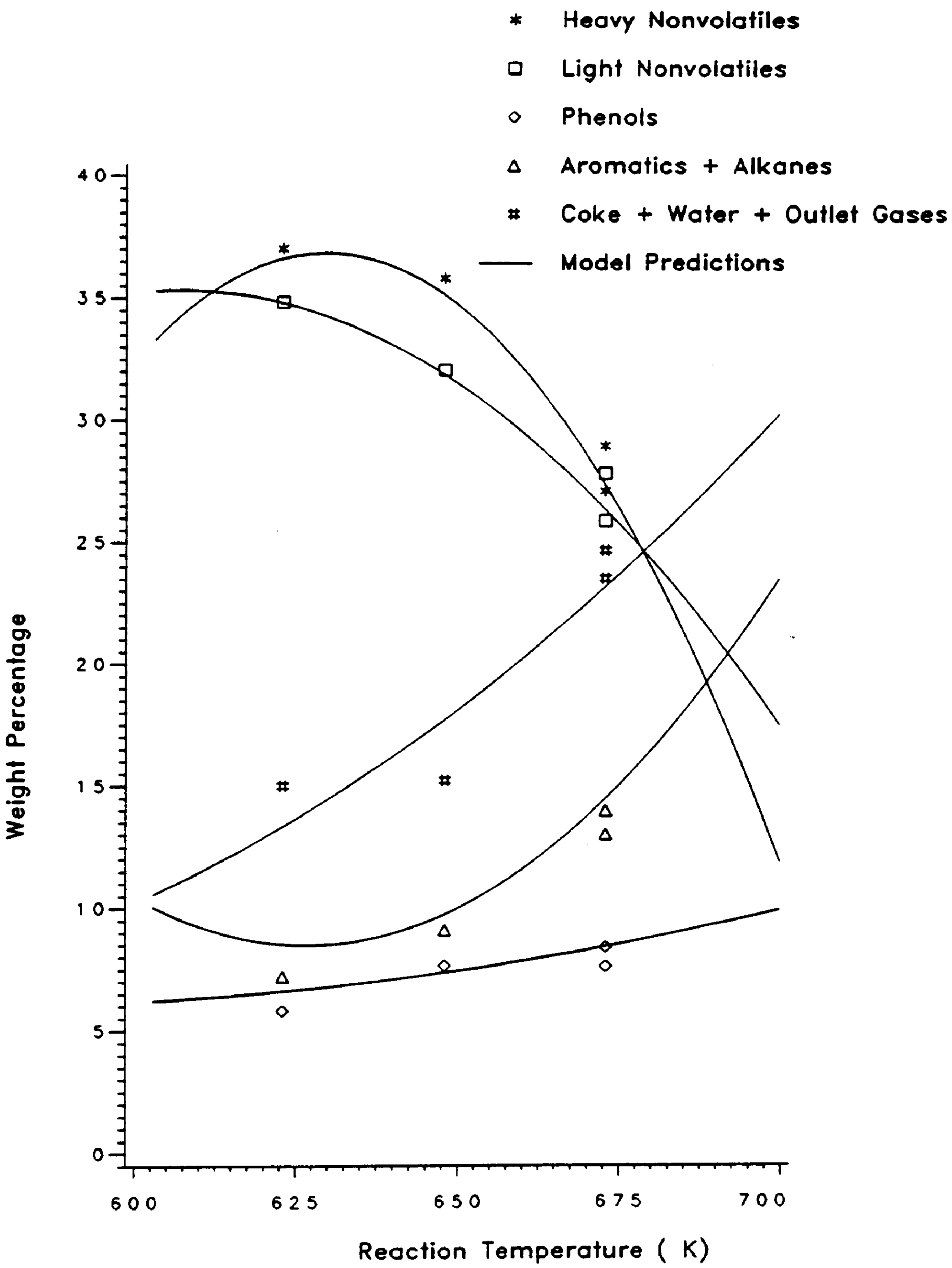

Figure 23. Temperature effect on hydrotreated pyrolytic oil product. Catalyst: CoMo, pressure: 8,720 kPa, WHSV: 2 hr^{-1}.

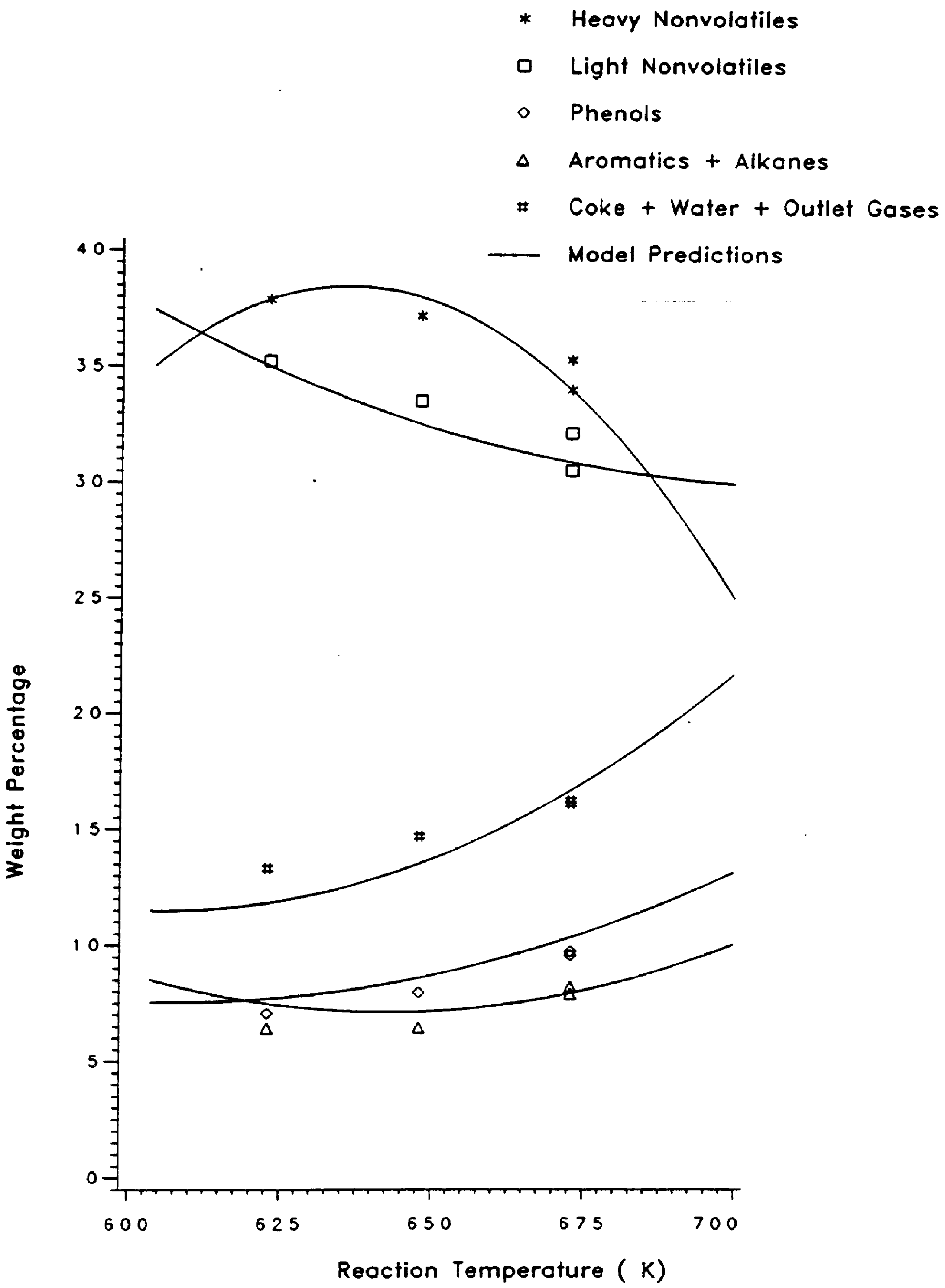

Figure 24. Temperature effect on hydrotreated pyrolytic oil product. Catalyst: NiMo, pressure: 8,720 kPa, WHSV: 2 hr^{-1}.

Table 14, one can observe that all the frequency factors increased with reaction pressure except the n_5 for Pt/Al_2O_3 catalyst. It means all the rate constants in the lumped kinetic model will increase with higher reaction pressure except in the following reaction using Pt/Al_2O_3 as catalyst:

$$\text{"Aromatics + alkanes"} \xrightarrow{K_5} \text{"Coke + } H_2O \text{ + outlet gases"}$$

which decreases with higher reaction pressure.

Table 14. Effect of reaction pressure on predicted frequency factor of the lumped kinetic model

Pressure Effect	Pt/Al_2O_3	CoMo	NiMo
n_1	1.35	0.83	0.16
n_2	0.40	0.71	0.17
n_3	1.58	0.93	0.31
n_4	1.08	0.73	0.25
n_5	-0.64	1.34	0.30

The experimental and predicted profiles for the various reacting species at 673 K are shown in Figures 25 through 27. The points in the Figures are the experimental data. The solid lines were calculated from the lumped kinetic model parameters listed in Table 13 and 14. The agreement between the experimental results and model predictions appears to be reasonably good. Overall, the increase in reaction pressure caused less "Heavy nonvolatiles" and "Light nonvolatiles", and more "Aromatics + alkanes". The increase in reaction pressure also caused a higher proportion of "Coke + H_2O + outlet gases" and "Phenols" in liquid products, accompanied by higher "Coke + H_2O + outlet gases" on the CoMo and NiMo catalysts, but less "Coke + H_2O + outlet gases" on the Pt/Al_2O_3.

Effect of Space Velocity

The effect of weight hourly space velocity on the reaction product was evaluated at 0.5, 1.0, 2.0, and 3.0 hr^{-1}. The experimental and predicted concentration profiles for the various reacting species using Pt/Al_2O_3, CoMo, and NiMo as reaction catalysts are shown in Figures 28, 29, and 30, respectively. Comparing Figures 28 through 30, one can observe:

(1) The weight percentage of phenols fraction does not vary with different space velocities. It means that at 673 K and 8720 kPa that the lumped reaction rate of "Light nonvolatiles $\longrightarrow$ Phenols" is equal to the reaction rate of "Phenols $\longrightarrow$ Aromatics + alkanes".

(2) The production of aromatics and alkanes favors low space velocity in Pt/Al_2O_3 catalyst.

(3) CoMo catalyst forms more "Coke + H_2O + outlet gases" during the hydrotreating reaction than Pt/Al_2O_3 or NiMo catalyst.

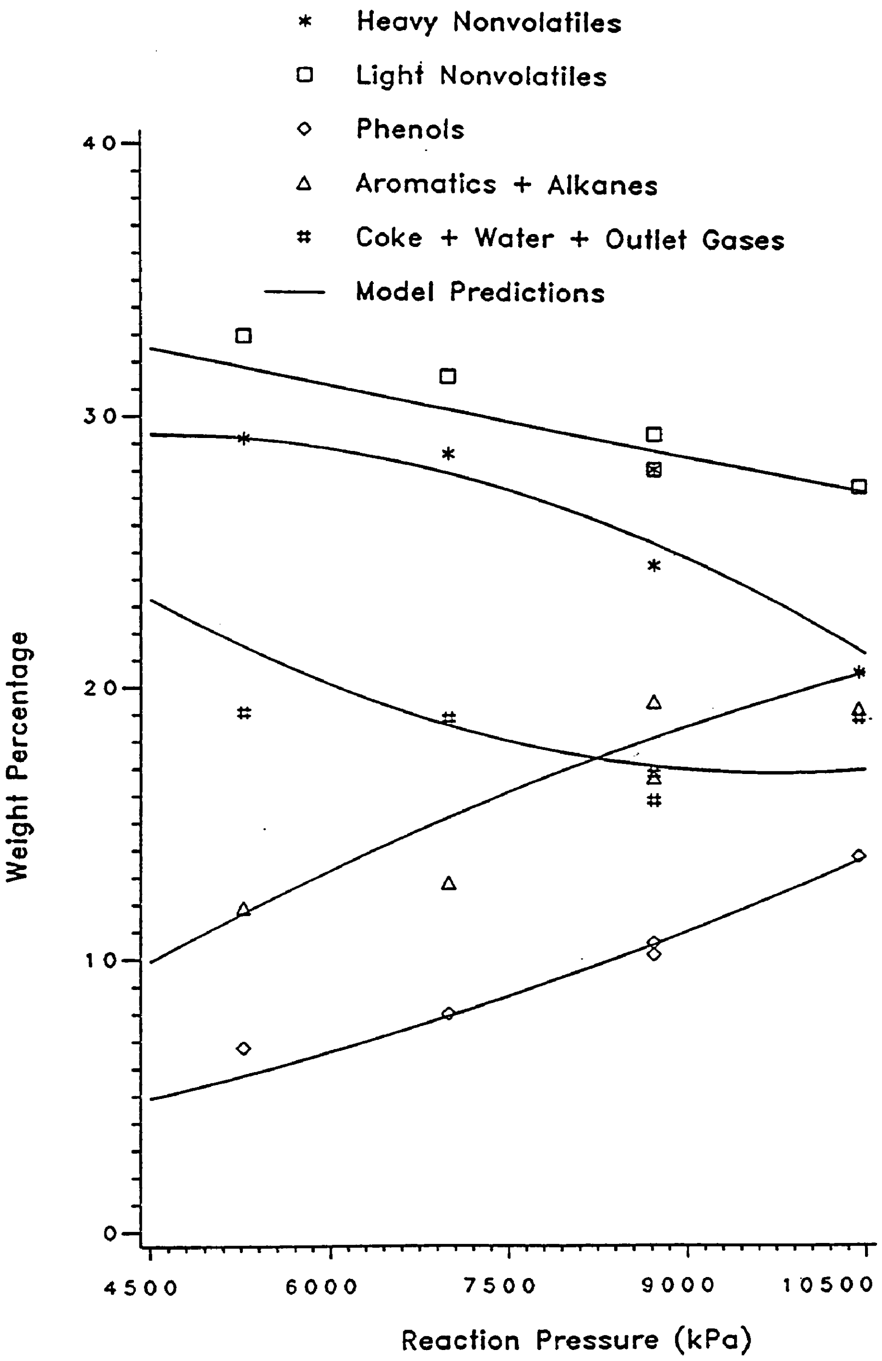

Figure 25. Pressure effect on hydrotreated pyrolytic oil product. Catalyst: Pt/Al_2O_3, WHSV: 2 hr^{-1}, temperature: 673 K.

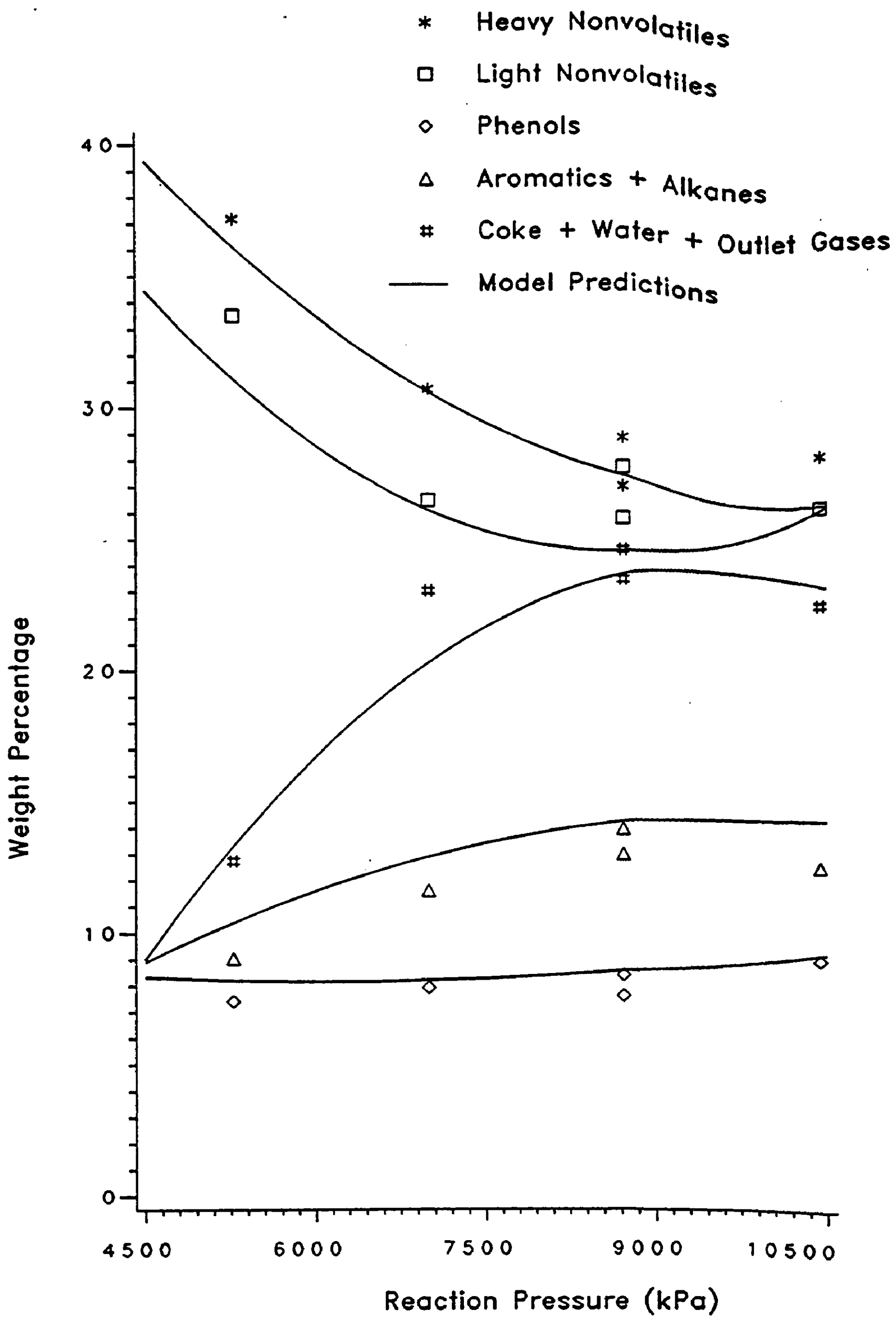

Figure 26. Pressure effect on hydrotreated pyrolytic oil product. Catalyst: CoMo, WHSV: 2 hr^{-1}, temperature: 673 K.

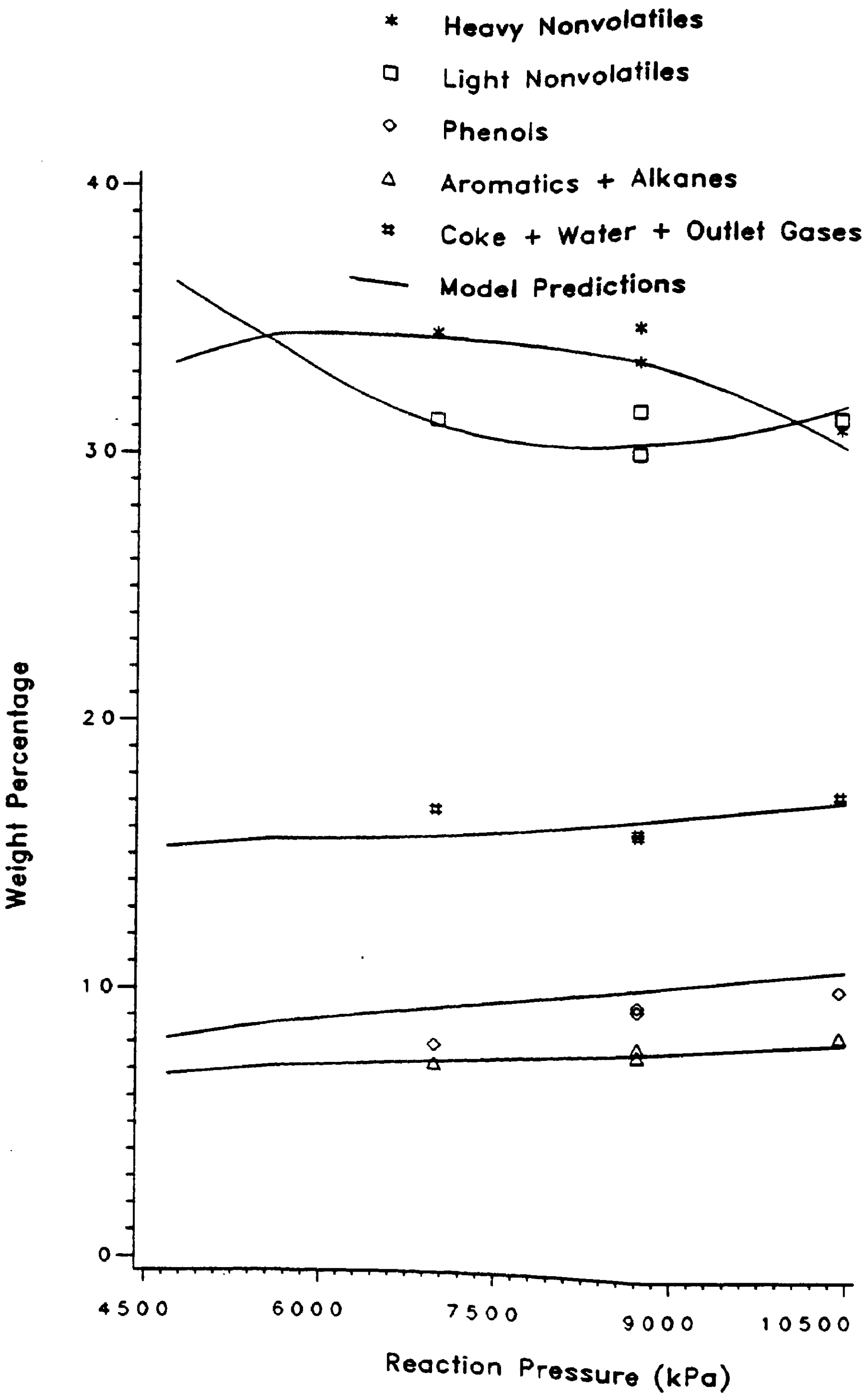

Figure 27. Pressure effect on hydrotreated pyrolytic oil product. Catalyst: NiMo, WHSV: 2 hr^{-1}, temperature: 673 K.

(4) For NiMo catalyst, the most significant changes in hydrotreated oil at different space velocities are the "Light nonvolatiles" and "Coke + H_2O +outlet gases" fractions.

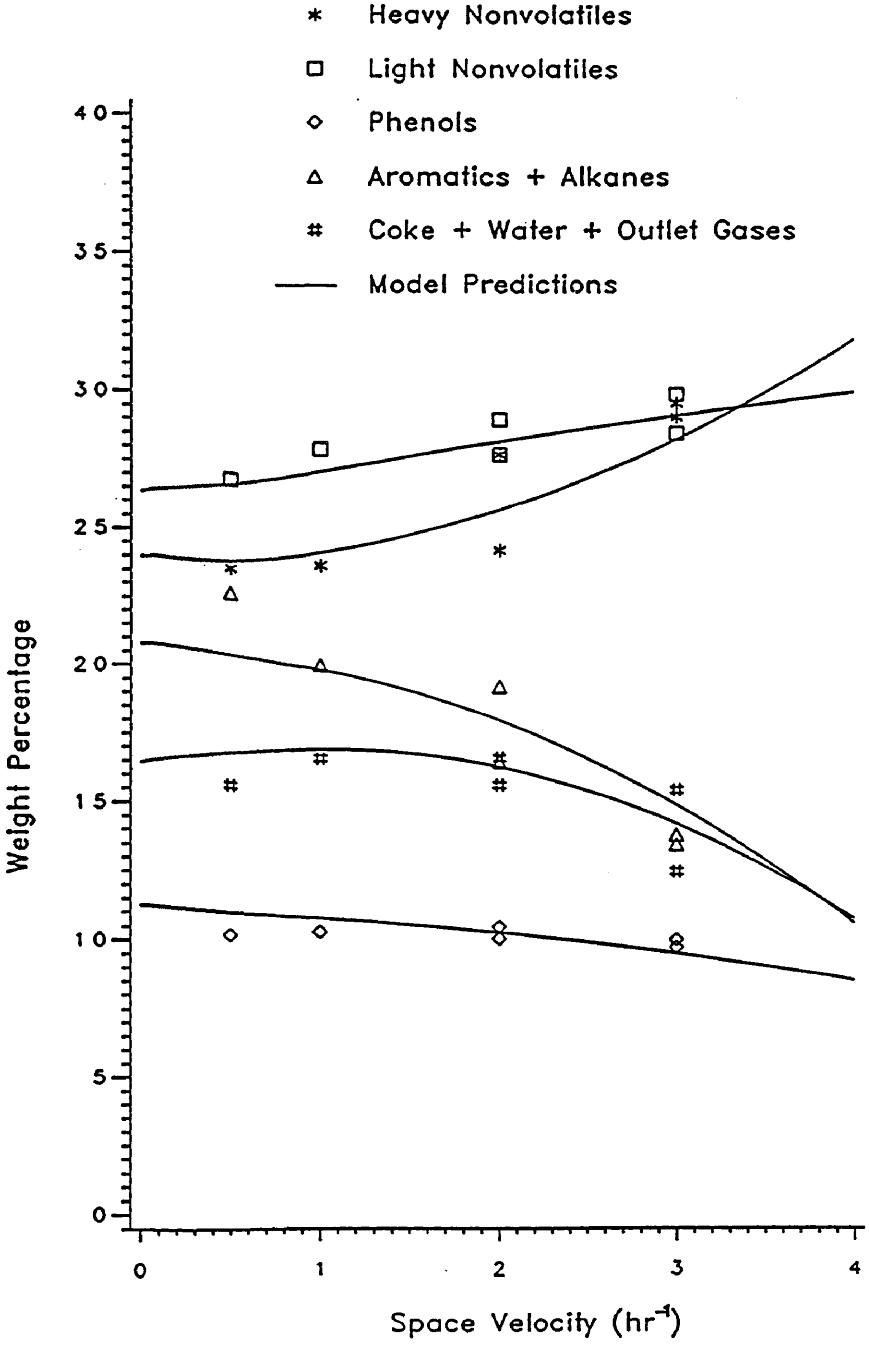

Figure 28. Space velocity effect on hydrotreated pyrolytic oil product. Catalyst: Pt/Al_2O_3, pressure: 8,720 kPa, temperature: 673 K.

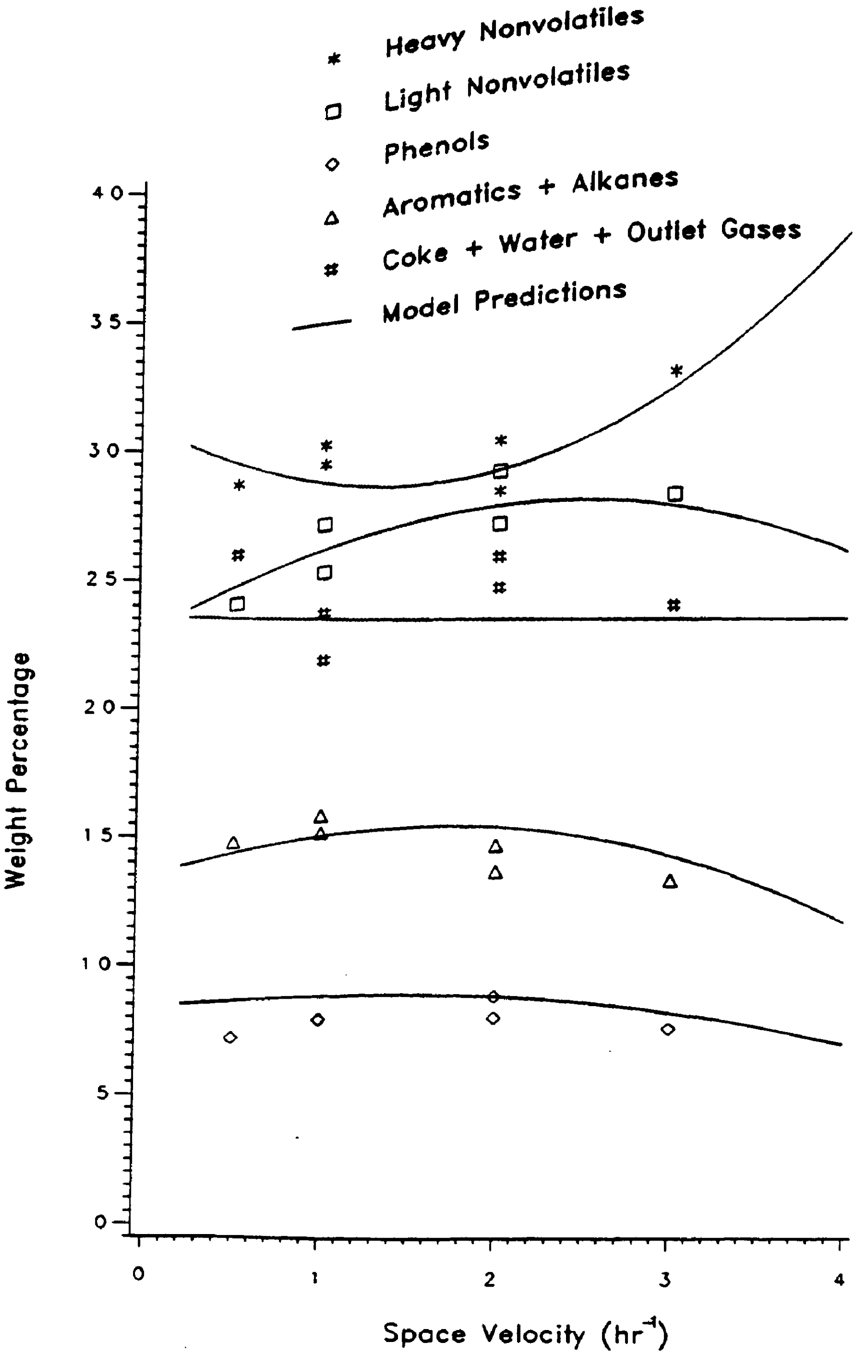

Figure 29. Space velocity effect on hydrotreated pyrolytic oil product. Catalyst: CoMo, pressure: 8,720 kPa, temperature: 673 K.

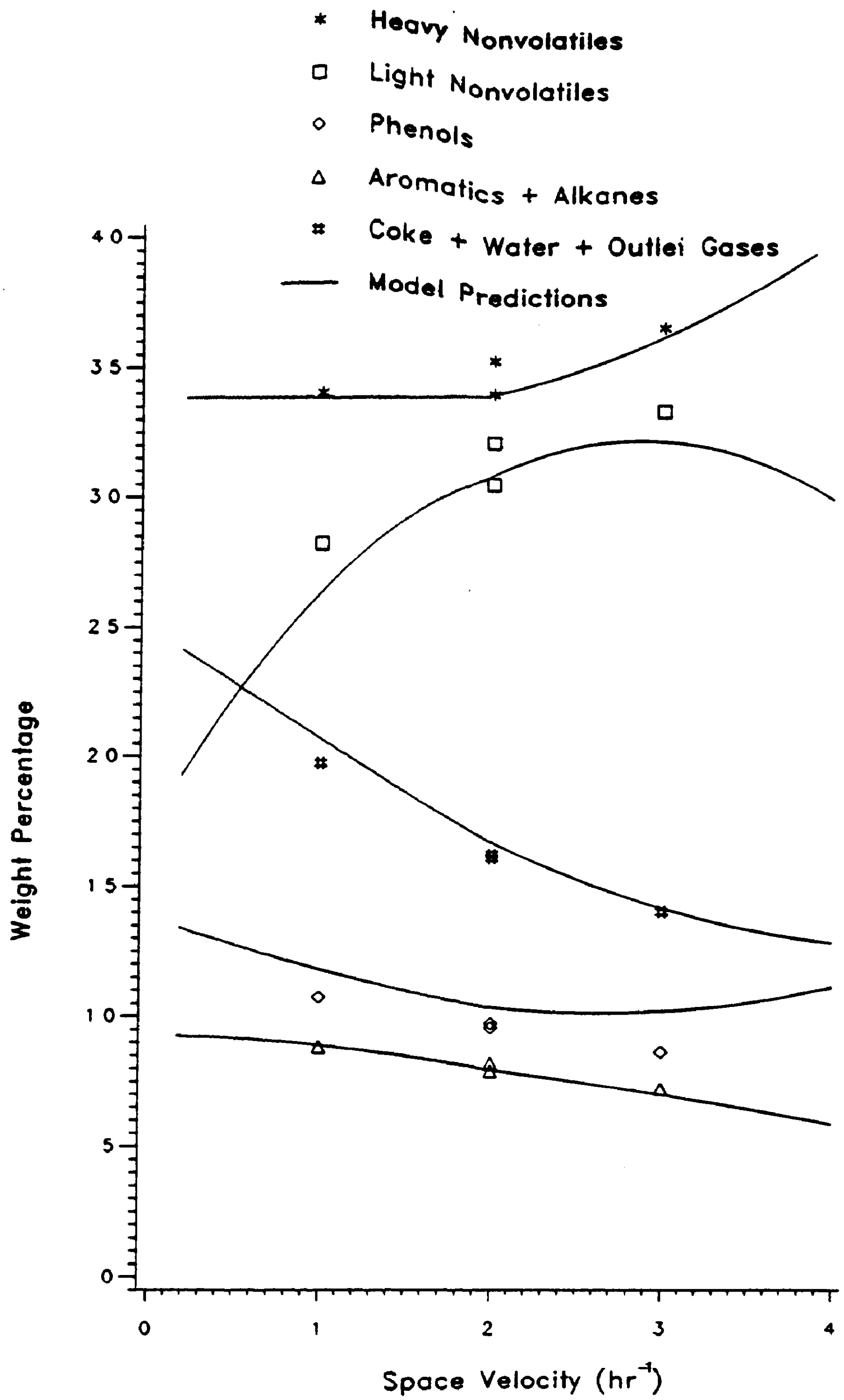

Figure 30. Space velocity effect on hydrotreated pyrolytic oil product. Catalyst: NiMo, pressure: 8,720 kPa, temperature: 673 K.

CHAPTER V

CONCLUSIONS

The SEC-GC separation scheme developed in this work is quite appropriate for studying the hydrotreating process of the pine pyrolytic oil which removes oxygen and converts the nonvolatiles and residual materials to lighter oils. SEC can separate the complex mixture into fractions, with similar functionalities. GC can determine the amount of volatiles in each fraction. The species which are in low concentration can be enriched and components which were masked by the bulk species in the GC can be freed by the SEC separation technique. Because the separation of fractions was made on an arbitrary basis, and limited to four or five fractions, slight overlapping of some species was observed. The combined use of SEC-GC allows one to monitor the compositional changes of pyrolytic oils during the hydrotreating reaction, and the SEC-GC analytical data can be used in the development of kinetic models.

Although the experimental data for oxygen removal shows the changes in space velocity did not have significant effect on oxygen removal, the "activation energies" developed from the oxygen removal model for CoMo and NiMo catalysts agree with those reported on literature. No kinetic data using Pt/Al_2O_3 as catalyst on oxygen removal has been reported in literature.

Data obtained from the SEC-GC analysis were modeled with pseudo first order kinetics describing the reaction rates of lumped species.

The model was composed of five fractions: (1) heavy nonvolatiles, (2) light nonvolatiles, (3) phenols, (4) aromatics + alkanes, and (5) coke + H_2 + outlet gases. An Arrhenius model was used to describe the temperature dependence of the rate constants. A clear trend of the effect of reaction temperature, weight hourly space velocity, and reaction pressure on hydrotreating pyrolytic oil using Pt/Al_2O_3, CoMo, and NiMo catalyst were observed. The agreements between the experimental data and model predictions are good. Small trickle-bed reactors such as those used in laboratories and pilot plants have some axial despersion. The Peclet number estimated from the lumped kinetic model is about 10.

The SEC-GC analysis of hydrotreated pyrolytic oil shows that part of the phenols in pine pyrolytic oil have been hydrotreated and converted into aromatics, and phenols also have been produced from the nonvolatiles during the reaction. Some aromatics were converted from the light nonvolatile fraction directly. The alkanes were produced by removing the oxygen atoms from the esters in the pine pyrolytic oil during the hydrotreating reaction.

Pt/Al_2O_3 catalyst has the best hydrotreating ability among the four catalysts tested. The reason for NiW catalyst did not succeed in the upgrading process is that NiW is a strong cracking catalyst, not a hydrotreating catalyst. During the upgrading process, some oxygen functional groups in the pyrolytic oil has to be removed (hydrotreated) first, otherwise the oxygen-containing compound in pyrolytic oil would polymerize at high temperature.

The hydrotreated product at the reaction conditions applied in this research still contain a certain amount of oxygen and nonvolatiles. In order to remove more oxygen and converted the nonvolatiles into volatiles, a higher reaction temperature and pressure or a new more efficient catalyst should be applied.

NOTATION

A_i = frequency factor (min^{-1})

C_{oxy} = concentration of oxygen in pyrolytic oil

$$= \frac{\text{gram of oxygen in hydrotreated oil}}{\text{gram of oxygen in raw pyrolytic oil}}$$

C^{o}_{oxy} = initial oxygen concentration (equal to one)

D = dispersion of the reacting species in liquid phase (cm^2/min)

D_T = reactor diameter (cm)

Da^{o}_{i} = Damkohler number

E_i = activation energy (kJ/g-mole)

K = rate constant = $A\ e^{-E/RT}$

m = reaction order

n = pressure effect order

P = reaction pressure (kPa)

Pe_M = Peclet number

R = gas constant

R_i = reaction rate of species "i"

T = reaction temperature (K)

T_o = reference temperature (K)

u_L = superficial velocity of the pyrolytic oil (cm/min)

w_i = Gauss Quadrature constants

X_{oxy} = oxygen conversion

$$Y_i = \frac{\text{density of reacting fraction "i"}}{\text{density of pine pyrolytic oil}}$$

Z_T = total catalytic bed length (cm)

Z = catalytic bed length (cm)

Greek Letters

ρ_B = bulk catalytic bed density

ρ_i = density of reacting species "i"

ρ_o = density of pine pyrolytic oil

$\gamma_i = \frac{E_i}{RT_o}$

LITERATURE CITED

Baltisverger, R. J., Klabunde, K. J., Stenberg V. Z., Woolsey, N. F., Saito, K., and Sukalski, W.. "Comparison of solvent refined lignites with solvent refined bituminous coal," *Am. Chem. Soc. Div. Fuel Chem. Reprints.* 22(5), 84, (1977).

Bowden, J. N., and Brinkman, D. W., "Stability Characteristics of Shale and Coal Liquids," DOE Report DOE/BETC/4162-10, (1980).

Chatterjee, A. K., "State-of-the-Art Review of Pyrolysis of Wood and Agricultural Biomass," Final Report, Contract No. 53-319-R-0-206, AC Project P0380, USDA Forest Service, Washington, D.C., (1981).

Cogswell, T. E., and Latham, D. R., "Chromatographic separation of coal liquid," *Am. Chem. Soc. Div. Preprints.* 23(2), 58, (1977).

de Rosset, A. J., Tan, G., and Gatsis J. G., "Upgrading primary coal liquids by hydrotreatment," *ACS, Advances in Chem Series.* 179, 109, (1979).

Dietz, W. A., "Response factor for gas chromatographic analysis," *J. of Gas Chromatography.* 5(2), 68, (1967).

Elder T. J., and Soltes, E. J., "Further Investigations into the Composition and Utility of a Commercial Wood Pyrolysis Oil," Paper presented at the American Chemical Society National Meeting, Honolulu, HI, (1979a).

Elder, T. J. and Soltes, E. J., "Adhesive Potentials of Some Phenolic Constituents of Pyrolytic Oil," Paper presented at the American Chemical Society National Meeting, Washington, D.C., (1979b).

Elder, T. J., and Soltes, E. J., "Pyrolysis of Lignocellulosic Materials : Characterization of the Phenolic Constituents of a Pine Pyrolytic Oil," *Wood & Fiber*, 12, 217, (1980).

Elder, T. J., "The Characterization and Potential Utilization of the Phenolic Compounds Found in a Pyrolytic Oil," Ph.D. Dissertation, Texas A&M University, (1979).

Elliott, D. C., "Hydrodeoxygenation of phenolic components of wood-derived oil," paper presented at the ACS Meeting, Seattle, WA, (1983).

Garten, R. L. and Ushiba, K. K., "Catalytic Conversion of Biomass to Fuel," DOE/ET/11013, (1980).

Givens, E. N., Collura, M. A., Skinner, R. W., and Greskovich, E. J., "Catalytic Hydroprocessing of Solvent-Refined Coal," *ACS, Advances in Chem Series*. 179, 121, (1979).

Haider, G., "Catalytic Hydrodeoxygenation of Coal-Derived Liquids and Related Oxygen Containing Compounds," Ph.D. Dissertation, The University of Utah, (1981).

Herskowitz, M., and Smith, J. M., "Trickle Bed Reactor : A Review," *AIChE J.*, 29(1), 1, (1983).

Jewell, D. M., Weber, J. H., Bunger, J. W., Plancher, H. and Latham, D. R., "Ion-exchange, coordination, and adsorption chromatographic separation of heavy-end petroleum distillates," *Anal. Chem.* 44, 1391, (1972).

Knight, J. A., Bowen, K. R., and Purdy K. R., "Pyrolysis - a Method for Conversion of Forestry Waste to Useful Fuel," paper presented at the Forest Products Research Society Meeting, Atlanta, GA, (1976).

Krishnamurthy, S., Panvelker, S., and Shah, Y. T., "Hydrodeoxygenation of Dibenzofuran and Related Compounds," *AIChE J.* 27(6), 994, (1981).

Lin, S. C., "Volatile Constituents in a Wood Pyrolysis Oil," M.S. thesis, Texas A&M University, (1978).

Lin, S. C., "Hydrocarbons via Catalytic Hydrogen Treatment of a Wood Pyrolytic Oil," Ph.D. Dissertation, Texas A&M University, (1981).

Philip, C. V., Anthony, R. G. and Zingaro, R. A., "Liquid sulfur dioxide as an agent for upgrading coal liquid," *Am. Chem. Soc. Symp.* 156, 239, (1981).

Philip, C. V., and Anthony, R. G., "Separation of coal-derived liquids by Gel Permeation Chromatography," *Am. Chem. Soc. Div. Fuel Chem. Preprints.* 24(3), 204, (1979).

Philip, C. V., and Anthony, R. G., "Separation of coal-derived liquids by Gel Permeation Chromatography," *Fuel*, 61, 357, (1982).

Philip, C. V., Bullin, J. A., and Anthony, R. G., "Analysis of Lignite-Derived Gases by Automated Gas Chromatography," *J. of Chromatograic Science*, 17, 523, (1979).

Reed, T. B., "Biomass Energy Refineries for Production of Fuel and Fertilizer," in Proc., 8th Cellulose Conf. I. Wood Chemicals, Wiley-Interscience, N.Y., (1975).

Rollmann, L. D., "Catalytic Hydrogenation of Model Nitrogen, Sulfur, and Oxygen Compounds," *J. of Catalysis*, 46, 243, (1977).

Satterfield, C. N., and Yang, S. H., "Simultaneous Hydrodenitrogenation and Hydrodeoxygenation of Model Compounds in a Trickle Bed reactor," *J. of Catalysis*, 81, 335, (1983).

Shah, Y. T., *Gas-Liquid-Solid Reactor Design*, McGraw-Hill Co., New York, NY, (1979).

Sheu, Y. E., Philip, C. V., Anthony, R. G., and Soltes, E. J., "Separation of Functionalities in Pyrolytic Tar by Gel Permeation Chromatography - Gas Chromatography," *J. of Chromatographic Science*, 22, 497, (1984).

Shultz, H., and Mima M. J., "Comparison of methods for determing asphaltenes in coal-derived liquid fuels," *Am. Chem. Soc. Div. Fuel Chem. Preprints*. 23(2), 76, (1978).

Soltes, E. J., and Elder, T. J., "Pyrolysis," *Organic Chemicals from Biomass*, (I. S. Goldstein, ed.) CRC Press Ins., Boca Raton, FL., (1981).

Soltes, E. J., and Lin, S. C., "Adhesives from Natural Resources," in *Progress in Biomass Conversion, Vol. 4*, Academic Press, New York, (1983a).

Soltes, E. J., and Lin, S. C., "Vehicular Fuels and Oxychemicals from Biomass Thermochemical Tars," *Biotech. Bioeng. Symp.* 5, 53, (1983b).

Soltes, E. J., and Lin, S. C., "Hydroprocessing of Biomass Tars for Liquid Engine Fuels," *Progress in Biomass Conversion*, 5, 1, (1984).

Soltes, E. J., "Biomass Pyrolysis," 1979 Texas Biomass Research Workshop, Texas A&M University, College Station, Texas, (1979).

Soltes, E. J., "Hydrocarbons from Lignocellulosic Residues," *J. of Appl. Polymer Sci.* 37, 775, (1983a).

Soltes, E. J., "Biomass Degradation Tars as Sources of Chemicals and Fuel Hydrocarbons," *Wood and Agricultural Residues: Research on Use for Feed, Fuels and Chemicals.* E.J. Soltes, editor, Academic Press, New York, NY, (1983b).

Tarng, Y. J., and Anthony, R. G., "Estimation of Parameters in Differential Equations," quarterly report, U. S. Department of Energy, DOE/FC/10601-4, March 31, (1984).

Ternan, M., and Brown, J. R., "Hydrotreating a Distillate Liquid derived from Subbituminous Coal using a Sulphided $CoO-MoO_3-Al_2O_3$ Catalyst," *Fuel*, 61, 1110, (1982).

APPENDIX A

EXPERIMENTAL DATA

The data shown in this Appendix summarize the experimental results for the reaction experiments and the analytic results by the SEC–GC method. No NiW/Al_2O_3 data are included. During all NiW/Al_2O_3 reactions, significant coke was formed which plugged the reactor and increased the system pressure gradually.

The inputs in material balance include liquid feed (pine pyrolytic oil plus decalin) and hydrogen gas feed. The hydrogen to pine pyrolytic oil feed ratio was maintained at a constant value of $4.16*10^{-3}$ gmole to 1 gram pyrolytic oil feed (640 cuft/ 1 barrel). The liquid feed was maintained at a constant ratio of 2 grams of decalin to 1 gram of pine pyrolytic oil. The outlet includes liquid product (excluding the water layer), outlet gas, water (water layer in liquid product), and coke deposited on the catalyst. The material balance was calculated based on one gram of pine pyrolytic oil plus two grams of decalin feed. The carbon, hydrogen, and oxygen composition in the hydrotreated oil was determined by elemental analysis. A sample calculation is given in Appendix B. The outlet gas was measured by wet test meter and its composition determined by GC analysis. The coke determined by the regeneration experiment represents the accumulated amount of coke that had been deposited on the catalyst during the run. The amount of gas and coke shown in the material balance are the total amount divided by the total pyrolytic oil input. The amount of H_2O is determined by separating and weighing the water layer in hydrotreated pyrolytic oil.

The WHSV was defined as:

$$\text{WHSV} = \frac{\text{Gram of pine pyrolytic oil input per hour}}{\text{Gram of catalyst in the reactor}}$$

Reaction No: 220

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 100 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6082	0.0778	0.1568
Solvent	1.7391	0.2609	0.0	1.7391	0.2382	0.0
Gas	0.0	0.0083	0.0	0.0012	0.0264	0.0014
Coke	0.0	0.0	0.0	0.0213	0.0043	0.0
Water	0.0	0.0	0.0	0.0	0.0074	0.0589
Total	2.3822	0.3456	0.2805	2.3698	0.3541	0.2171

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	4.45	0.0	4.45
2	23.38	3.27	20.12
3	28.95	10.63	18.32
4	27.35	16.25	11.10
Total	84.13	30.15	53.98

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	24.57
2	Light Nonvolatiles:	29.41
3	Volatile Phenols:	10.63
4	Aromatics:	16.25
5	Alkanes:	3.27
6	Gas + H_2O + Coke:	15.87

Reaction No: 308

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 85 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6091	0.0761	0.1463
Solvent	1.7391	0.2609	0.0	1.7391	0.2329	0.0
Gas	0.0	0.0083	0.0	0.0012	0.0352	0.0017
Coke	0.0	0.0	0.0	0.0279	0.0056	0.0
Water	0.0	0.0	0.0	0.0	0.0089	0.0709
Total	2.3822	0.3456	0.2805	2.3773	0.3587	0.2189

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	4.95	0.0	4.95
2	25.63	2.47	23.16
3	28.17	10.19	17.98
4	24.39	14.25	10.14
Total	83.14	26.91	56.23

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	28.11
2	Light Nonvolatiles:	28.12
3	Volatile Phenols:	10.19
4	Aromatics:	14.25
5	Alkanes:	2.47
6	Gas + H_2O + Coke:	16.86

Reaction No: 313

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 1.0 hr^{-1}

Run Time: 95 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6028	0.0845	0.1439
Solvent	1.7391	0.2609	0.0	1.7391	0.2186	0.0
Gas	0.0	0.0083	0.0	0.0088	0.0292	0.0022
Coke	0.0	0.0	0.0	0.0329	0.0051	0.0
Water	0.0	0.0	0.0	0.0	0.0117	0.0935
Total	2.3822	0.3456	0.2805	2.3836	0.3491	0.2396

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	3.96	0.0	3.96
2	23.30	3.23	20.07
3	27.72	10.45	17.27
4	28.15	17.09	11.06
Total	83.13	30.77	52.36

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	24.03
2	Light Nonvolatiles:	28.33
3	Volatile Phenols:	10.45
4	Aromatics:	17.09
5	Alkanes:	3.23
6	Gas + H_2O + Coke:	16.87

Reaction No: 318

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 3.0 hr^{-1}

Run Time: 49 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5569	0.0721	0.1142
Solvent	1.7391	0.2609	0.0	1.7391	0.2423	0.0
Gas	0.0	0.0083	0.0	0.0009	0.0181	0.0012
Coke	0.0	0.0	0.0	0.0381	0.0028	0.0
Water	0.0	0.0	0.0	0.0	0.0089	0.0714
Total	2.3822	0.3456	0.2805	2.3150	0.3442	0.1868

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.78	0.0	1.78
2	23.77	1.51	22.26
3	28.02	10.15	17.87
4	20.74	10.67	10.07
Total	74.31	22.33	51.98

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	24.04
2	Light Nonvolatiles:	27.94
3	Volatile Phenols:	10.15
4	Aromatics:	10.67
5	Alkanes:	1.51
6	Gas + H_2O + Coke:	25.69

Reaction No: 321

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 623 K

Pressure: 8,720 kPa WHSV: 3.0 hr^{-1}

Run Time: 55 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6159	0.0598	0.2101
Solvent	1.7391	0.2609	0.0	1.7391	0.2565	0.0
Gas	0.0	0.0083	0.0	0.0048	0.0318	0.0032
Coke	0.0	0.0	0.0	0.0336	0.0037	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0
Total	2.3822	0.3456	0.2805	2.3934	0.3518	0.2133

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	5.03	0.0	5.03
2	31.77	2.30	29.47
3	29.44	6.46	22.98
4	22.22	8.51	13.71
Total	88.46	17.27	71.19

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	34.50
2	Light Nonvolatiles:	36.69
3	Volatile Phenols:	6.46
4	Aromatics:	8.51
5	Alkanes:	2.30
6	Gas + H_2O + Coke:	11.54

Reaction No: 325

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 623 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 68 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6057	0.0660	0.2034
Solvent	1.7391	0.2609	0.0	1.7391	0.2339	0.0
Gas	0.0	0.0083	0.0	0.0009	0.0202	0.00118
Coke	0.0	0.0	0.0	0.0568	0.0063	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0
Total	2.3822	0.3456	0.2805	2.4025	0.3264	0.2045

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	6.42	0.0	6.42
2	29.83	1.90	27.93
3	27.97	6.94	21.03
4	23.35	9.87	13.48
Total	87.57	18.71	68.86

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	34.35
2	Light Nonvolatiles:	34.51
3	Volatile Phenols:	6.94
4	Aromatics:	9.87
5	Alkanes:	1.90
6	Gas + H_2O + Coke:	12.43

Reaction No: 328

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 0.5 hr^{-1}

Run Time: 190 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6255	0.0886	0.1479
Solvent	1.7391	0.2609	0.0	1.7391	0.2269	0.0
Gas	0.0	0.0083	0.0	0.0010	0.0250	0.0018
Coke	0.0	0.0	0.0	0.0380	0.0053	0.0
Water	0.0	0.0	0.0	0.0	0.0140	0.1123
Total	2.3822	0.3456	0.2805	2.4036	0.3598	0.2620

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.74	0.0	2.74
2	25.69	4.59	21.10
3	27.18	10.32	16.86
4	28.58	18.33	10.25
Total	84.19	33.24	50.95

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	23.84
2	Light Nonvolatiles:	27.11
3	Volatile Phenols:	10.32
4	Aromatics:	18.33
5	Alkanes:	4.59
6	Gas + H_2O + Coke:	15.81

Reaction No: 401

Reaction Condition:

Catalyst: Pt/Al_2O_3	Salt Bath Temperature: 623 K
Pressure: 8,720 kPa	WHSV: 2.0 hr^{-1}
Run Time: 85 mins.	

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6094	0.0632	0.2064
Solvent	1.7391	0.2609	0.0	1.7391	0.2449	0.0
Gas	0.0	0.0083	0.0	0.0012	0.0352	0.0018
Coke	0.0	0.0	0.0	0.0492	0.0059	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0
Total	2.3822	0.3456	0.2805	2.3989	0.3492	0.2082

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	5.95	0.0	5.95
2	31.04	2.99	28.03
3	29.04	6.53	22.51
4	21.87	7.89	13.98
Total	87.88	17.41	70.47

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	33.98
2	Light Nonvolatiles:	36.49
3	Volatile Phenols:	6.53
4	Aromatics:	7.89
5	Alkanes:	2.99
6	Gas + H_2O + Coke:	12.12

Reaction No: 418

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 5,272 kPa WHSV: 2.0 hr^{-1}

Run Time: 80 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5847	0.0666	0.2009
Solvent	1.7391	0.2609	0.0	1.7391	0.2426	0.0
Gas	0.0	0.0083	0.0	0.0004	0.0188	0.0003
Coke	0.0	0.0	0.0	0.0249	0.0041	0.0
Water	0.0	0.0	0.0	0.0	0.0070	0.0560
Total	2.3822	0.3456	0.2805	2.3491	0.3391	0.2572

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	6.25	0.0	6.25
2	23.76	0.79	22.97
3	28.51	6.77	21.74
4	22.38	11.13	11.25
Total	80.90	18.69	62.21

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	29.22
2	Light Nonvolatiles:	32.99
3	Volatile Phenols:	6.77
4	Aromatics:	11.13
5	Alkanes:	0.79
6	Gas + H_2O + Coke:	19.10

Reaction No: 420

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 10,443 kPa WHSV: 2.0 hr^{-1}

Run Time: 60 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6090	0.0722	0.1304
Solvent	1.7391	0.2609	0.0	1.7391	0.2538	0.0
Gas	0.0	0.0083	0.0	0.0005	0.0219	0.0010
Coke	0.0	0.0	0.0	0.0190	0.0039	0.0
Water	0.0	0.0	0.0	0.0	0.0155	0.1241
Total	2.3822	0.3456	0.2805	2.3676	0.3673	0.2555

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.31	0.0	2.31
2	22.50	4.22	18.28
3	29.71	13.80	15.91
4	26.57	15.03	11.54
Total	81.09	33.05	48.04

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	20.59
2	Light Nonvolatiles:	27.45
3	Volatile Phenols:	13.80
4	Aromatics:	15.03
5	Alkanes:	4.22
6	Gas + H_2O + Coke:	18.91

Reaction No: 423

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 648 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 90 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5982	0.0775	0.1782
Solvent	1.7391	0.2609	0.0	1.7391	0.2484	0.0
Gas	0.0	0.0083	0.0	0.0007	0.0246	0.0008
Coke	0.0	0.0	0.0	0.0428	0.0025	0.0
Water	0.0	0.0	0.0	0.0	0.0076	0.0610
Total	2.3822	0.3456	0.2805	2.3808	0.3606	0.2400

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	5.01	0.0	5.01
2	27.12	1.17	25.95
3	30.46	8.59	21.87
4	22.80	10.80	12.00
Total	85.39	20.56	64.83

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	30.96
2	Light Nonvolatiles:	33.87
3	Volatile Phenols:	8.59
4	Aromatics:	10.80
5	Alkanes:	1.17
6	Gas + H_2O + Coke:	14.61

Reaction No: 502

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 6,996 kPa WHSV: 2.0 hr^{-1}

Run Time: 70 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5588	0.0771	0.1751
Solvent	1.7391	0.2609	0.0	1.7391	0.2383	0.0
Gas	0.0	0.0083	0.0	0.0009	0.0196	0.0063
Coke	0.0	0.0	0.0	0.0311	0.0049	0.0
Water	0.0	0.0	0.0	0.0	0.0073	0.0582
Total	2.3822	0.3456	0.2805	2.3699	0.3472	0.2396

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	4.82	0.0	4.82
2	25.56	1.69	23.87
3	28.07	8.02	20.05
4	22.65	11.16	11.49
Total	81.10	20.87	60.23

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	28.69
2	Light Nonvolatiles:	31.54
3	Volatile Phenols:	8.02
4	Aromatics:	11.16
5	Alkanes:	1.69
6	Gas + H_2O + Coke:	18.90

Reaction No: 508

Reaction Condition:

Catalyst: Pt/Al_2O_3 Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 3.0 hr^{-1}

Run Time: 48 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.6150	0.0750	0.1521
Solvent	1.7391	0.2609	0.0	1.7391	0.2530	0.0
Gas	0.0	0.0083	0.0	0.0007	0.0159	0.0015
Coke	0.0	0.0	0.0	0.0378	0.0047	0.0
Water	0.0	0.0	0.0	0.0	0.0073	0.0587
Total	2.3822	0.3456	0.2805	2.3926	0.3569	0.2123

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	4.40	0.0	4.40
2	28.29	2.65	25.64
3	30.18	9.89	20.29
4	21.45	11.37	10.08
Total	84.32	23.91	60.31

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	30.04
2	Light Nonvolatiles:	30.37
3	Volatile Phenols:	9.89
4	Aromatics:	11.37
5	Alkanes:	2.65
6	Gas + H_2O + Coke:	15.68

Reaction No: 516

Reaction Condition:

Catalyst: CoMo　Salt Bath Temperature: 673 K

Pressure: 8,720 kPa　WHSV: 2.0 hr^{-1}

Run Time: 60 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5476	0.0632	0.1634
Solvent	1.7391	0.2609	0.0	1.7391	0.2562	0.0
Gas	0.0	0.0083	0.0	0.0006	0.0157	0.0005
Coke	0.0	0.0	0.0	0.0934	0.0064	0.0
Water	0.0	0.0	0.0	0.0	0.0078	0.0628
Total	2.3822	0.3456	0.2805	2.3807	0.3493	0.2267

Upgraded Pyrolytic Oil Analysis by SEC—GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.76	0.0	1.76
2	27.35	0.13	27.22
3	24.79	7.62	17.17
4	23.57	12.89	10.68
Total	77.47	20.64	56.83

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	28.98
2	Light Nonvolatiles:	27.85
3	Volatile Phenols:	7.62
4	Aromatics:	12.89
5	Alkanes:	0.13
6	Gas + H_2O + Coke:	23.53

Reaction No: 518

Reaction Condition:

Catalyst: CoMo Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 95 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5215	0.0572	0.1671
Solvent	1.7391	0.2609	0.0	1.7391	0.2590	0.0
Gas	0.0	0.0083	0.0	0.0009	0.0150	0.0004
Coke	0.0	0.0	0.0	0.0723	0.0056	0.0
Water	0.0	0.0	0.0	0.0	0.0099	0.0793
Total	2.3822	0.3456	0.2805	2.3266	0.3467	0.2468

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.59	0.0	1.59
2	25.85	0.32	25.53
3	24.61	8.41	16.20
4	23.37	13.67	9.70
Total	75.32	22.40	52.90

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	27.12
2	Light Nonvolatiles:	25.90
3	Volatile Phenols:	8.41
4	Aromatics:	13.67
5	Alkanes:	0.32
6	Gas + H_2O + Coke:	24.68

Reaction No: 521

Reaction Condition:

Catalyst: CoMo | Salt Bath Temperature: 673 K

Pressure: 8,720 kPa | WHSV: 1.0 hr^{-1}

Run Time: 134 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5552	0.0675	0.1636
Solvent	1.7391	0.2609	0.0	1.7391	0.2566	0.0
Gas	0.0	0.0083	0.0	0.0012	0.0196	0.0015
Coke	0.0	0.0	0.0	0.1077	0.0075	0.0
Water	0.0	0.0	0.0	0.0	0.0096	0.0765
Total	2.3822	0.3456	0.2805	2.4032	0.3608	0.2416

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.33	0.0	1.33
2	27.65	0.17	27.48
3	24.81	7.80	17.01
4	24.84	15.32	9.52
Total	78.63	23.29	55.34

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	28.81
2	Light Nonvolatiles:	26.53
3	Volatile Phenols:	7.80
4	Aromatics:	15.32
5	Alkanes:	0.17
6	Gas + H_2O + Coke:	21.37

Reaction No: 526

Reaction Condition:

Catalyst: CoMo Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 0.5 hr^{-1}

Run Time: 185 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5019	0.0679	0.1725
Solvent	1.7391	0.2609	0.0	1.7391	0.2560	0.0
Gas	0.0	0.0083	0.0	0.0004	0.0128	0.0005
Coke	0.0	0.0	0.0	0.0916	0.0068	0.0
Water	0.0	0.0	0.0	0.0	0.0093	0.0748
Total	2.3822	0.3456	0.2805	2.3330	0.3528	0.2478

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	0.94	0.0	0.94
2	28.34	0.79	27.55
3	21.77	7.15	14.62
4	23.17	13.90	9.27
Total	74.22	20.84	53.38

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	28.49
2	Light Nonvolatiles:	23.89
3	Volatile Phenols:	7.15
4	Aromatics:	13.90
5	Alkanes:	0.79
6	Gas + H_2O + Coke:	25.78

Reaction No: 528

Reaction Condition:

Catalyst: CoMo	Salt Bath Temperature: 623 K
Pressure: 8,720 kPa	WHSV: 2.0 hr^{-1}
Run Time: 62 mins.	

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5391	0.0723	0.2261
Solvent	1.7391	0.2609	0.0	1.7391	0.2560	0.0
Gas	0.0	0.0083	0.0	0.0011	0.0151	0.0004
Coke	0.0	0.0	0.0	0.0924	0.0059	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0
Total	2.3822	0.3456	0.2805	2.3717	0.3493	0.2265

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	5.39	0.0	5.39
2	31.68	0.0	31.68
3	30.78	5.82	24.96
4	17.12	7.22	9.90
Total	84.97	13.04	71.93

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	37.07
2	Light Nonvolatiles:	34.86
3	Volatile Phenols:	5.82
4	Aromatics:	7.22
5	Alkanes:	0.0
6	Gas + H_2O + Coke:	15.03

Reaction No: 611

Reaction Condition:

Catalyst: CoMo Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 1.0 hr^{-1}

Run Time: 116 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5314	0.0616	0.1753
Solvent	1.7391	0.2609	0.0	1.7391	0.2574	0.0
Gas	0.0	0.0083	0.0	0.0006	0.0159	0.0004
Coke	0.0	0.0	0.0	0.0883	0.0068	0.0
Water	0.0	0.0	0.0	0.0	0.0091	0.0725
Total	2.3822	0.3456	0.2805	2.3594	0.3508	0.2482

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.73	0.0	1.73
2	29.27	1.47	27.80
3	23.03	7.76	15.27
4	22.81	13.36	9.45
Total	76.84	22.59	54.25

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	29.53
2	Light Nonvolatiles:	24.72
3	Volatile Phenols:	7.76
4	Aromatics:	13.36
5	Alkanes:	1.47
6	Gas + H_2O + Coke:	23.16

Reaction No: 616

Reaction Condition:

Catalyst: CoMo   Salt Bath Temperature: 673 K

Pressure: 8,720 kPa   WHSV: 3.0 hr^{-1}

Run Time: 60 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5343	0.0668	0.1724
Solvent	1.7391	0.2609	0.0	1.7391	0.2501	0.0
Gas	0.0	0.0083	0.0	0.0004	0.0161	0.0007
Coke	0.0	0.0	0.0	0.0805	0.0051	0.0
Water	0.0	0.0	0.0	0.0	0.0081	0.0648
Total	2.3822	0.3456	0.2805	2.3543	0.3462	0.2379

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.57	0.0	2.57
2	28.96	0.39	28.57
3	23.47	7.11	16.36
4	22.42	12.14	10.28
Total	77.42	19.64	57.78

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	31.14
2	Light Nonvolatiles:	26.64
3	Volatile Phenols:	7.11
4	Aromatics:	12.14
5	Alkanes:	0.39
6	Gas + H_2O + Coke:	22.58

Reaction No: 621

Reaction Condition:

Catalyst: CoMo　Salt Bath Temperature: 673 K

Pressure: 6,996 kPa　WHSV: 2.0 hr^{-1}

Run Time: 60 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5088	0.0670	0.1736
Solvent	1.7391	0.2609	0.0	1.7391	0.2579	0.0
Gas	0.0	0.0083	0.0	0.0004	0.0171	0.0009
Coke	0.0	0.0	0.0	0.1155	0.0068	0.0
Water	0.0	0.0	0.0	0.0	0.0063	0.0504
Total	2.3822	0.3456	0.2805	2.3638	0.3551	0.2249

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	3.28	0.0	3.28
2	28.41	0.89	27.52
3	24.42	7.94	16.48
4	20.81	10.73	10.08
Total	76.92	21.56	55.36

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	30.80
2	Light Nonvolatiles:	26.56
3	Volatile Phenols:	7.94
4	Aromatics:	10.73
5	Alkanes:	0.89
6	Gas + H_2O + Coke:	23.08

Reaction No: 719

Reaction Condition:

Catalyst: CoMo Salt Bath Temperature: 648 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 48 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5600	0.0674	0.2201
Solvent	1.7391	0.2609	0.0	1.7391	0.2602	0.0
Gas	0.0	0.0083	0.0	0.0011	0.0151	0.0005
Coke	0.0	0.0	0.0	0.1087	0.0070	0.0
Water	0.0	0.0	0.0	0.0	0.0037	0.0296
Total	2.3822	0.3456	0.2805	2.4089	0.3534	0.2502

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	3.59	0.0	3.59
2	32.28	0.0	32.28
3	29.64	7.66	21.98
4	19.24	9.12	10.12
Total	84.75	16.78	67.97

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	35.87
2	Light Nonvolatiles:	32.10
3	Volatile Phenols:	7.66
4	Aromatics:	9.12
5	Alkanes:	0.0
6	Gas + H_2O + Coke:	15.25

Reaction No: 722

Reaction Condition:

Catalyst: CoMo   Salt Bath Temperature: 673 K

Pressure: 5,272 kPa   WHSV: 2.0 hr^{-1}

Run Time: 52 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5883	0.0724	0.1844
Solvent	1.7391	0.2609	0.0	1.7391	0.2586	0.0
Gas	0.0	0.0083	0.0	0.0003	0.0151	0.0006
Coke	0.0	0.0	0.0	0.0873	0.0062	0.0
Water	0.0	0.0	0.0	0.0	0.0041	0.0328
Total	2.3822	0.3456	0.2805	2.4150	0.3502	0.2178

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.62	0.0	1.62
2	36.19	0.59	35.60
3	30.45	7.43	23.02
4	18.99	8.47	10.52
Total	87.25	16.49	70.76

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	37.22
2	Light Nonvolatiles:	33.54
3	Volatile Phenols:	7.43
4	Aromatics:	8.47
5	Alkanes:	0.59
6	Gas + H_2O + Coke:	12.75

Reaction No: 725

Reaction Condition:

Catalyst: CoMo　　Salt Bath Temperature: 673 K

Pressure: 10,443 kPa　　WHSV: 2.0 hr^{-1}

Run Time: 55 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5299	0.0708	0.1708
Solvent	1.7391	0.2609	0.0	1.7391	0.2578	0.0
Gas	0.0	0.0083	0.0	0.0012	0.0151	0.0005
Coke	0.0	0.0	0.0	0.0787	0.0045	0.0
Water	0.0	0.0	0.0	0.0	0.0071	0.0568
Total	2.3822	0.3456	0.2805	2.3489	0.3533	0.2281

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.11	0.0	1.11
2	28.88	1.37	27.51
3	24.42	9.14	15.28
4	22.73	11.36	11.37
Total	77.14	21.87	55.27

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	28.62
2	Light Nonvolatiles:	26.65
3	Volatile Phenols:	9.14
4	Aromatics:	11.36
5	Alkanes:	1.37
6	Gas + H_2O + Coke:	22.86

Reaction No: 828

Reaction Condition:

Catalyst: NiMo Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 40 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5615	0.0652	0.1983
Solvent	1.7391	0.2609	0.0	1.7391	0.2605	0.0
Gas	0.0	0.0083	0.0	0.0002	0.0132	0.0004
Coke	0.0	0.0	0.0	0.0821	0.0067	0.0
Water	0.0	0.0	0.0	0.0	0.0046	0.0368
Total	2.3822	0.3456	0.2805	2.3829	0.3502	0.2355

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.23	0.0	2.23
2	33.10	0.0	33.10
3	31.78	9.75	22.03
4	16.75	8.22	8.53
Total	83.86	17.97	65.89

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	35.33
2	Light Nonvolatiles:	30.56
3	Volatile Phenols:	9.75
4	Aromatics:	8.22
5	Alkanes:	0.0
6	Gas + H_2O + Coke:	16.14

Reaction No: 902

Reaction Condition:

Catalyst: NiMo Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 48 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5312	0.0663	0.2021
Solvent	1.7391	0.2609	0.0	1.7391	0.2603	0.0
Gas	0.0	0.0083	0.0	0.0003	0.0138	0.0005
Coke	0.0	0.0	0.0	0.0792	0.0063	0.0
Water	0.0	0.0	0.0	0.0	0.0053	0.0424
Total	2.3822	0.3456	0.2805	2.3498	0.3520	0.2450

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.78	0.0	1.78
2	32.62	0.35	32.27
3	32.80	9.60	23.20
4	16.53	7.56	8.97
Total	83.73	17.51	66.22

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	34.05
2	Light Nonvolatiles:	32.17
3	Volatile Phenols:	9.60
4	Aromatics:	7.56
5	Alkanes:	0.35
6	Gas + H_2O + Coke:	16.27

Reaction No: 904

Reaction Condition:

Catalyst: NiMo Salt Bath Temperature: 673 K

Pressure: 8,720 kPa WHSV: 1.0 hr^{-1}

Run Time: 154 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5405	0.0636	0.1965
Solvent	1.7391	0.2609	0.0	1.7391	0.2597	0.0
Gas	0.0	0.0083	0.0	0.0005	0.0144	0.0006
Coke	0.0	0.0	0.0	0.0842	0.0050	0.0
Water	0.0	0.0	0.0	0.0	0.0056	0.0448
Total	2.3822	0.3456	0.2805	2.3642	0.3483	0.2419

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.32	0.0	2.32
2	31.22	0.0	31.22
3	29.96	10.55	19.41
4	17.08	8.68	8.40
Total	80.58	19.23	61.35

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	33.54
2	Light Nonvolatiles:	27.81
3	Volatile Phenols:	10.55
4	Aromatics:	8.68
5	Alkanes:	0.0
6	Gas + H_2O + Coke:	19.42

Reaction No: 908

Reaction Condition:

Catalyst: NiMo　　Salt Bath Temperature: 673 K

Pressure: 10,443 kPa　　WHSV: 2.0 hr^{-1}

Run Time: 74 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5573	0.0725	0.1991
Solvent	1.7391	0.2609	0.0	1.7391	0.2597	0.0
Gas	0.0	0.0083	0.0	0.0003	0.0138	0.0004
Coke	0.0	0.0	0.0	0.0862	0.0054	0.0
Water	0.0	0.0	0.0	0.0	0.0047	0.03769
Total	2.3822	0.3456	0.2805	2.3829	0.3423	0.2371

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	1.60	0.0	1.60
2	30.53	0.67	29.86
3	30.19	10.34	19.85
4	20.01	7.99	12.02
Total	82.33	19.00	63.33

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	31.46
2	Light Nonvolatiles:	31.87
3	Volatile Phenols:	10.34
4	Aromatics:	7.99
5	Alkanes:	0.65
6	Gas + H_2O + Coke:	17.67

Reaction No: 910

Reaction Condition:

Catalyst: NiMo	Salt Bath Temperature: 673 K

Pressure: 8,720 kPa	WHSV: 3.0 hr^{-1}

Run Time: 42 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5612	0.0696	0.2068
Solvent	1.7391	0.2609	0.0	1.7391	0.2604	0.0
Gas	0.0	0.0083	0.0	0.0002	0.0130	0.0003
Coke	0.0	0.0	0.0	0.0752	0.0055	0.0
Water	0.0	0.0	0.0	0.0	0.0034	0.0272
Total	2.3822	0.3456	0.2805	2.3757	0.3519	0.2343

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.26	0.0	2.26
2	34.39	0.0	34.39
3	31.83	8.65	23.18
4	17.46	7.22	10.24
Total	85.94	15.87	70.07

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	36.65
2	Light Nonvolatiles:	33.42
3	Volatile Phenols:	8.65
4	Aromatics:	7.22
5	Alkanes:	0.0
6	Gas + H_2O + Coke:	14.06

Reaction No: 912

Reaction Condition:

Catalyst: NiMo Salt Bath Temperature: 648 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 76 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5499	0.0681	0.2322
Solvent	1.7391	0.2609	0.0	1.7391	0.2601	0.0
Gas	0.0	0.0083	0.0	0.0002	0.0128	0.0003
Coke	0.0	0.0	0.0	0.1079	0.0051	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0
Total	2.3822	0.3456	0.2805	2.3971	0.3461	0.2325

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.30	0.0	2.30
2	35.16	0.22	34.94
3	31.05	7.99	23.06
4	16.76	6.24	10.52
Total	85.27	14.45	70.82

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	37.24
2	Light Nonvolatiles:	33.58
3	Volatile Phenols:	7.99
4	Aromatics:	6.24
5	Alkanes:	0.24
6	Gas + H_2O + Coke:	14.73

Reaction No: 914

Reaction Condition:

Catalyst: NiMo Salt Bath Temperature: 623 K

Pressure: 8,720 kPa WHSV: 2.0 hr^{-1}

Run Time: 60 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5657	0.0656	0.2362
Solvent	1.7391	0.2609	0.0	1.7391	0.2597	0.0
Gas	0.0	0.0083	0.0	0.0002	0.0121	0.0002
Coke	0.0	0.0	0.0	0.0809	0.0066	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0
Total	2.3822	0.3456	0.2805	2.3859	0.3440	0.2364

Upgraded Pyrolytic Oil Analysis by SEC–GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	5.94	0.0	5.94
2	31.96	0.0	31.96
3	30.95	7.08	23.87
4	17.81	6.44	11.37
Total	86.66	13.52	73.14

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	37.90
2	Light Nonvolatiles:	35.24
3	Volatile Phenols:	7.08
4	Aromatics:	6.44
5	Alkanes:	0.0
6	Gas + H_2O + Coke:	13.34

Reaction No: 917

Reaction Condition:

Catalyst: NiMo　　Salt Bath Temperature: 673 K

Pressure: 6,996 kPa　　WHSV: 2.0 hr^{-1}

Run Time: 80 mins.

Material Balance (per gram of pyrolytic oil feed):

	Input (gram)			Output (gram)		
	C	H	O	C	H	O
Pyrolytic Oil	0.6431	0.0764	0.2805	0.5527	0.0695	0.1984
Solvent	1.7391	0.2609	0.0	1.7391	0.2585	0.0
Gas	0.0	0.0083	0.0	0.0003	0.0147	0.0004
Coke	0.0	0.0	0.0	0.0865	0.0044	0.0
Water	0.0	0.0	0.0	0.0	0.0042	0.0336
Total	2.3822	0.3456	0.2805	2.3786	0.3513	0.2324

Upgraded Pyrolytic Oil Analysis by SEC-GC (excluding the solvent):

Fraction	% of Feed	Volatiles in Fraction (% of feed)	Nonvolatiles in Fraction (% of feed)
1	2.41	0.0	2.41
2	32.91	0.0	32.91
3	30.26	8.14	22.12
4	17.32	7.45	9.87
Total	82.90	15.59	67.31

Lumped Fractions For Kinetic Modelling (wt. %):

1	Heavy Nonvolatiles:	35.32
2	Light Nonvolatiles:	31.99
3	Volatile Phenols:	8.14
4	Aromatics:	7.45
5	Alkanes:	0.0
6	Gas + H_2O + Coke:	17.10

APPENDIX B

SAMPLE CALCULATION FOR DETERMINATION OF C.H.O. COMPOSITION IN HYDROTREATED PYROLYTIC OIL

Carbon, hydrogen, and oxygen amounts in upgraded pyrolytic oil are calculated as shown in the following steps:

Step 1: Determine the amount and composition of solvents in the hydrotreated pyrolytic oil. From the GC analysis of GPC fraction 5 (solvent fraction) of the hydrotreated product one can obtain the weight of the solvents (decalin, tetralin, and naphthalene). Equation (25) shows the reactions among the solvents.

$$C_{10}H_{18} \longleftrightarrow C_{10}H_{12} + 3H_2 \longleftrightarrow C_{10}H_8 + 2H_2 \tag{25}$$

The total moles of solvents does not change during the reaction, so one can calculate the corresponding amount of decalin input by equation (26).

$$\frac{W_1}{138} + \frac{W_2}{132} + \frac{W_3}{128} = \frac{\text{Decalin Input}}{138} \tag{26}$$

where:

W_1 = wt. of the decalin in upgraded oil.

W_2 = wt. of the tetralin in upgraded oil.

W_3 = wt. of the naphthalene in upgraded oil.

138 = molecular weight of decalin.

132 = molecular weight of tetralin.

128 = molecular weight of naphthalene.

Step 2: Liquid yield of pyrolytic oil is defined as follows:

$$\text{Liquid Yield} = \frac{\Sigma(\text{wt. of fractions by GPC–GC}) - (\text{solvents in upgraded oil})}{\text{pine pyrolytic oil input}} \qquad (27)$$

The Σ(wt. of fractions by GPC–GC) represents the weight of liquid product which includes the hydrotreated oil and solvents. The liquid reactants input into the reactor were at a ratio of 2 grams of decalin to 1 gram of pine pyrolytic oil.

thus:

$$\frac{\text{decalin input}}{2} = \text{pine pyrolytic oil input}$$

Step 3: Determine the C, H, and O weight % in liquid product (which including solvents) by elemental analysis.

Step 4: Substract the C and H contributed by the solvents from the liquid product. Then, one can get the C, H, and O compositions in the hydrotreated pyrolytic oil.

Sample Calculation

Reaction No.: 220

Step 1: Solvents in upgraded oil determined by GC analysis.

From GC analysis of the Reaction No. 220 product, one can obtain:

decalin:	0.09616	89.90%
tetralin:	0.00666	6.23%
naphthalene:	0.00414	3.87%
TOTAL:	0.10696 grams	100.00%

Apply equation (26):

$$\frac{0.09616}{138} + \frac{0.00666}{132} + \frac{0.00414}{128} = \frac{\text{decalin input}}{138}$$

decalin input = 0.107586 grams

Thus, for each 0.107586 grams decalin input into the reaction, 0.10696 grams solvent mixtures has been produced. Therefore, for 2 grams of decalin input, the solvent yield (decalin + tetralin + naphthalene) is:

$$\frac{0.10696}{0.107586} * 2 = 1.98836 \text{ grams.}$$

The 0.01164 grams lost in solvent is due to the release of H_2 during the reaction as shown in equation (25).

Step 2: Determine the liquid yield. The weight of each fraction separated by the GPC method is listed below:

GPC fraction No.	weight (grams)
1	0.0024
2	0.0127
3	0.0156
4	0.0106
5	0.1110
Total	0.1523

Applying equation (27):

$$\text{Liquid Yield} = \frac{0.1523 - 0.10696}{0.107586/2} * 100 = 84.28\ \%$$

Thus, for each 2 grams of decalin and 1 gram pine pyrolytic oil input, the liquid reaction product is 1.98836 grams solvent plus 0.8428 grams hydrotreated oil.

Step 3:The C, H, and O weight % in upgraded liquid product (which includs solvents) determined by elemental analysis are listed below:

	weight (%)
Carbon	: 82.91 %
Hydrogen	: 11.55 %
Oxygen	: 5.54 %

For 2 grams decalin and 1 gram pine pyrolytic oil input, the liquid product is 2.83116 gram (1.98836 gram solvents and 0.8428 gram upgraded oil). The weight composition of the hydrotreated liquid product is:

	weight grams
Carbon	: 2.34731
Hydrogen	: 0.32701
Oxygen	: 0.15684

Step 4: Substract the C and H contributed by the solvents in the hydrotreated liquid product.

C and H contributed by the solvents:

	C	H
decalin	1.55438	0.233157
tetralin	0.11261	0.011261
naphthalene	0.07214	0.004810
Total	1.73912	0.249228

Substract the C and H in the solvents (step 4) from the total C, H, and O (step 3), one can get the composition of the upgraded oil based on one gram of pine pyrolytic oil input.

Carbon	: 0.60819 grams
Hydrogen	: 0.07777 grams
Oxygen	: 0.15684 grams

APPENDIX C

COEFFICIENTS FOR THE TEMPERATURE PROFILE INSIDE THE REACTOR

The reaction temperature which measured inside the reactor as a function of Z was found by curve fitting the axial temperature profile by a fourth order polynomial:

$$T = a_o + a_1Z + a_2Z^2 + a_3Z^3 + a_4Z^4 \ (°C) \qquad (29)$$

The coefficients (a_o, a_1, a_2, a_3, and a_4) for the reaction temperature profile inside the reactor are listed in this Appendix.

Reaction No.	a_0	a_1	a_2	a_3	a_4
220	187.96950192	39.61976325	−2.37236769	0.04739194	−9.1171547E−05
308	189.78542140	41.09109398	−2.38083414	0.01918447	0.00118239
313	197.94517716	57.87349893	−6.03997639	0.26743372	−0.00423279
318	195.68949125	14.79487296	2.71287787	−0.30979257	0.00816687
321	177.95970343	16.83358534	1.79757291	−0.24648826	0.00683381
325	184.79299171	10.46114897	2.91462107	−0.31491941	0.00822297
328	203.48378866	64.38321845	−7.57850643	0.37670955	−0.00668540
401	189.30528422	22.47350329	0.25515857	−0.13121012	0.00414434
418	189.04358360	34.29831697	−0.86781174	−0.08457814	0.00341011
420	195.83744281	37.24190369	−1.75664323	−0.01589730	−0.00181557
423	192.24129474	33.72897467	−2.04820337	0.05558459	−0.00058163
502	192.98359299	29.10074185	−0.90868520	−0.04043512	0.00177091
508	208.36322682	48.57261575	−4.42599136	0.17363336	−0.00249146
516	176.54910085	55.15701744	−4.69201386	0.16207579	−0.00188511
518	176.75843031	50.77574443	−3.70508025	0.09425536	−0.00043010
521	188.14493162	53.07776408	−4.90305206	0.19657025	−0.00287271
526	196.58620479	65.48269594	−7.71947604	0.38562455	−0.00687865
528	182.98772559	16.11575214	1.28230644	−0.17206586	0.00439279
611	188.54529127	58.35963114	−6.04594263	0.27312682	−0.00450592
616	177.49992154	47.54496842	−3.32606599	0.08161146	−0.00034231
621	180.87846814	35.74833826	−1.56872450	−0.00846787	0.00122159
722	196.58571356	66.38917801	−7.72836967	0.37916682	−0.00663903
822	186.08765239	48.41419154	−3.77756083	0.11905214	−0.00122756
902	188.47109558	45.86968373	−3.38424973	0.09673281	−0.00080546
904	196.88786539	67.36014104	−8.23804631	0.42494108	−0.00777172
908	188.57719717	51.28729701	−4.43341287	0.16164571	−0.00209549
910	183.45177674	43.32093369	−2.89006166	0.06874608	−0.00029245
912	185.86932055	24.88023110	−0.22749066	−0.07189055	0.00222384
914	183.36309055	18.63439514	0.73893262	−0.13573597	0.00361696
917	174.15483958	56.06116900	−5.08314762	0.19772679	−0.00278417

APPENDIX D

NONLINEAR REGRESSION PROGRAM FOR DETERMINATION OF THE PARAMETERS IN OXYGEN REMOVAL

```
//REG JOB (B275,007A,S40,001,RA),'ED SHEU',MSGLEVEL=(0,0)
//*FORMAT PR,DDNAME=,DEST=XEROX,FORMS=1100
// EXEC SAS,REGION=512K
DATA TEMP;
INPUT  A B C D F L YA PR;
TO=613;
ZT=19.0;
R=1.9872;
W1=0.4679139346;
W2=0.4679139346;
W3=0.3607615730;
W4=0.3607615730;
W5=0.1713244924;
W6=0.1713244924;
E1=0.2386191861;
E2=-0.2386191861;
E3=0.6612093865;
E4=-0.6612093865;
E5=0.9324695142;
E6=-0.9324695142;
Z1=ZT/2+ZT/2*E1;
Z2=ZT/2+ZT/2*E2;
Z3=ZT/2+ZT/2*E3;
Z4=ZT/2+ZT/2*E4;
Z5=ZT/2+ZT/2*E5;
Z6=ZT/2+ZT/2*E6;
C1=1-TO/(273.16+(A+B*Z1+C*Z1**2+D*Z1**3+F*Z1**4));
C2=1-TO/(273.16+(A+B*Z2+C*Z2**2+D*Z2**3+F*Z2**4));
C3=1-TO/(273.16+(A+B*Z3+C*Z3**2+D*Z3**3+F*Z3**4));
C4=1-TO/(273.16+(A+B*Z4+C*Z4**2+D*Z4**3+F*Z4**4));
C5=1-TO/(273.16+(A+B*Z5+C*Z5**2+D*Z5**3+F*Z5**4));
C6=1-TO/(273.16+(A+B*Z6+C*Z6**2+D*Z6**3+F*Z6**4));
Y=60*1*.2806/.9978162;
Y=Y*1.E-9;
ZT=ZT*2.54;
CARDS;
*;
PROC NLIN BEST=10 DATA=TEMP METHOD=MARQUARDT;
 PARMS KO=0.1 TO 2.1 BY .5
       N=1 TO 2.1 BY 0.5
       M=0.1 TO 1.1 BY 0.5
       E=10000 TO 20000 BY 2000;
       EO=EXP(E/(R*TO));
 MODEL Y=KO*1.E-9*ZT/2*(W1*EO**C1+W2*EO**C2+W3*EO**C3+W4*EO**C4
 +W5*EO**C5+W6*EO**C6)*(PR**N)*((M-1)/(YA**(1-M)-1));
OUTPUT OUT=DATA2 PREDICTED=P1 RESIDUAL=R1;
*;
DATA DPLOT;
 SET DATA2(KEEP=YA Y P1 R1 L );
P=P1*1.E9 ;
Y=Y*1.E9 ;
R1=R1*1.E9;
```

```
PROC PRINT;
PROC PLOT; PLOT Y*YA='O' P*YA='*' /OVERLAY;
PROC PLOT; PLOT Y*P='O'/OVERLAY;
PROC PLOT;PLOT R1*YA='*'/VREF=0;
//*END
```