

**CATALYTIC CONVERSION OF BIOMASS-DERIVED OILS TO
FUELS AND CHEMICALS**

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To my wife Flora and daughter Fraikua for their
sacrifice, encouragement and love

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ABSTRACT

Experimental and kinetic modeling studies were carried out on the conversion a wood-oil obtained from high pressure liquefaction of aspen poplar wood to liquid hydrocarbon fuels and useful chemicals in a fixed bed micro-reactor using HZSM-5 catalyst. Similar experiments were conducted using silicalite, H-mordenite, H-Y and amorphous silica-alumina catalysts.

Preliminary vacuum distillation studies showed that the wood-oil was made up of volatile and non-volatile fractions. A maximum yield of 62 wt% volatiles at 200 °C, 172 Pa was obtained. The volatile fraction consisted of over 80 compounds. These compounds were comprised of acids, alcohols, aldehydes, ketones, esters, ethers, furans, phenols and some hydrocarbons. The characteristics of the oil showed that it was unstable with time, i.e., its physical properties and chemical composition changed with time probably due to the reaction of free radicals or the oxidative coupling of some of the wood-oil components. However, when the oil was mixed with tetralin, the stability improved.

Upgrading studies were first conducted over inert berl saddles in the presence and absence of steam (i.e. non-catalytic treatment/blank runs). Yields of hydrocarbons were between 16 and 25 wt% of the wood-oil. High residue fractions of between 32 to 56 wt% were obtained after processing. Some portions of wood-oil formed a carbonaceous material (char or coke) when exposed to the experimental temperatures. The chars (coke) fraction increased with temperature from 4.7 to 12.5 wt% when processing with steam and 8.0 to 20.4 wt% when processing without steam.

Catalytic upgrading studies were first carried out using

HZSM-5 catalyst in the presence and absence of steam. The results showed that approximately 40 to 65 wt% of the oil could be converted to a hydrocarbon-rich product (i.e. desired organic liquid product (distillate)). This contained about 45 to 70 wt% hydrocarbons with selectivities ranging between 0.47 to 0.88. This fraction was highly aromatic in nature and consisted mainly of benzene, toluene, xylene (BTX compounds) and other alkylated benzenes within the gasoline boiling point range. The yield and selectivities were strong functions of the process time and temperature. A comparison between the two processes, i.e. upgrading in the presence and absence of steam, showed that about 30 to 45 % reduction in coke formation and 5 to 18 wt% increase in organic distillate could be achieved when processing in the presence of steam. These changes were probably due to changes in the rates of cracking, deoxygenation, aromatization and polymerization reactions resulting from the competitive adsorption processes between steam and wood-oil molecules in addition to changes in contact time of molecules. However, the selectivity for hydrocarbons decreased in the presence of steam.

Yields of organic distillate fractions of between 72 to 93 wt% and hydrocarbon yields and selectivities of 44 to 51 wt% and 0.93 to 1.13, respectively, were obtained when wood-oil volatile fraction was upgraded over HZSM-5 after separation from the non-volatile fraction by vacuum distillation.

The spent HZSM-5 catalyst could be easily regenerated and reused with little change in its performance.

The yields and selectivities for hydrocarbons when upgrading with the other catalysts were between 9 and 22 wt%, and 0.12 and 0.29, respectively for silicalite, 16 and 28 wt%, and 0.22 and 0.28, respectively for H-mordenite, 15.5 and 21

wt%, and 0.17 and 0.21, respectively for H-Y and 8.5 and 26.2, and 0.13 and 0.36, respectively for silica-alumina. Compared to HZSM-5 (yield between 34 and 43 wt%, selectivity of 0.66 to 0.88) these yields and selectivities were much lower. These experiments also showed that the pore size, acidity and shape selectivity of the catalyst influenced the distribution of hydrocarbons in terms of the carbon number. The yield and selectivity of H-mordenite and H-Y (large pore zeolites) were mostly for kerosene range hydrocarbons (C₉ to C₁₅) and for silicalite and HZSM-5 (medium pore zeolites) for gasoline range hydrocarbons. The hydrocarbon fraction from amorphous silica-alumina did not show any defined distribution. The performance followed the order: HZSM-5 > H-mordenite > H-Y > Silicalite, Silica-alumina.

With the aid of model compound reactions involving acetic acid methyl ester, propanoic acid, 4-methylcyclohexanol, methylcyclopentanone, 2-methylcyclopentanone, methoxybenzene, ethoxybenzene, phenol, 2-methoxy-4-(2-propenyl)phenol, a synthetic and wood-oil volatile, two reaction pathways were proposed to explain the chemical steps through which the final products of upgrading were obtained. Also, reaction pathways were proposed for each chemical group. These experiments showed that the final products were formed probably through cracking, deoxygenation, olefin formation, oligomerization, hydrogen and hydride transfer, cyclization, isomerization, alkylation and polymerization reactions.

Rate models were derived based upon the two reaction pathways and the power law rate model. The rates of formation of products followed the general order: Organic distillate > Hydrocarbons > Residue > Coke > Gas > Aqueous Fraction. Estimates of the values of the kinetic parameters showed that the rate constants ranged between 10⁻⁶ (aqueous fraction) and 1.81 (volatile fraction), activation energies between 6.7-76.0 x

10^3 KJ/Kmol and reaction orders from 0.7 (gas formation) to 2.5 (residue formation). Two mathematical models were derived based on the integral reactor design equation and on the two reaction pathways. This was used to estimate the yield of products. The models predicted the experimental results fairly accurately. Model discrimination showed that the model based on coke and residue formation from both volatile and non-volatile fractions of the wood-oil best predicted the experimental results.

Hydrocarbon selectivity relations which were based on coke, residue and combined coke and residue as undesired products were also derived. Application of these relations showed that lower temperatures and concentrations were most appropriate for higher hydrocarbon selectivity. However, this was at the expense of higher conversions.

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NOMENCLATURE

| | |
|-------------|--|
| A | Constant |
| C | Concentration, Kmol/m^3 |
| c_p | Specific heat capacity, KJ/Kg K |
| d | Interlayer spacing |
| D_{ea} | Effective diffusivity, $\text{m}^3/\text{m h}$ |
| E | Activation energy, KJ/Kmol |
| EHI | Effective hydrogen index |
| F | Flowrate, Kmol/h |
| $-\Delta H$ | Heat of reaction, KJ/Kmol |
| H/C | Hydrogen to carbon ratio |
| H | Hydrocarbons |
| K | Reaction rate constant, adsorption rate constant |
| K_0 | Preexponential factor |
| n | Integer |
| O/C | Oxygen to carbon ratio |
| r | Rate of reaction, Kmol/kg.cat h |
| R | Gas constant, KJ/Kmol.K |
| S | Selectivity |
| t | Time, h |
| T | Temperature, $^{\circ}\text{C}$, K |
| U | Overall heat transfer coefficient, $\text{KJ/m}^2 \text{ h } ^{\circ}\text{C}$ |
| UA | Unaccounted fraction |
| UC | Unconverted feed or reactant |
| U_s | Superficial velocity, $\text{m}^3/\text{m}^2\text{h}$ |
| W | Weight of catalyst |

- X Conversion
y Yield
Z Axial coordinate in reactor

Superscripts

- a Reaction order for aqueous fraction formation path,
reaction order
A Reactant A
b Reaction order
B Reactant B
c Reaction order for coke formation path
cr Reaction order for cracking path
d Reaction order for organic distillate formation path
exp Experimental value
g Reaction order for gas formation path
h Reaction order for hydrocarbon formation path
nv Reaction order for non-volatiles formation path
p constant
r Reaction order for residue formation path
v Reaction order for volatiles formation path
y Predicted value from model

Subscripts

- A Aqueous fraction
ave Average
C Coke

Cr Cracking pathway

D Desired product, Organic distillate, Divergence from experimental values defined by equation 4.26

G Gas fraction

H Hydrocarbons

i Component, products, inlet

NV Non-volatiles

o outlet or exit

p Product, predicted value from model

R Residue

r surroundings

s superficial

UD Undesired product

V Volatiles

W Wood-oil

Greek Symbols

θ Wavelength of incident rays

λ_{ea} Effective thermal conductivity in a packed bed in axial direction

ρ_B Catalyst bulk density, Kg cat./m³

ϵ Void fraction of packing

Φ Fractional coverage

1. INTRODUCTION

Energy from fossil fuel sources forms a vital part of the transportation and process industries. However, the continuous use of these energy sources have created two global problems which have impelled researchers and industry to pursue research to explore alternative sources.

The diminishing supplies of low cost "non-renewable" fossil fuel and chemical feedstocks is one of the major problems. These sources are being consumed without replacement. The solution to this problem partly lies in the use of wood which represents a readily available and "renewable" source of energy. Wood, when processed to the appropriate liquid and gaseous forms, can serve as an alternative feedstock (to some extent) for the fuels and chemicals industries.

The second problem which has generated a lot of public outcry and political concern, especially within the recent decade, concerns the effects of acid rain and dioxins and the global warming effect of CO₂ [Hayes, 1989; Haughton, 1990; Tollefson, 1992] on the environment. The burning of fossil fuels and the use of related chemicals introduce gases such as carbon dioxide (CO₂), chlorofluorocarbons and methane into the atmosphere. These gases distribute themselves throughout the atmosphere, trapping infra red radiation leaving the earth's surface and causing the so called "green-house effect", a

condition where the earth's temperature rises above the normal. It is well known that the carbon in fossil-fuel sources has been stored for millions of years and therefore adds to the load of carbon dioxide when burnt. The net annual release of CO₂ has been reported [Haughton, 1990] to be approximately 3×10^{15} g. In contrast, biomass is "CO₂-neutral", i.e. it releases as much CO₂ when burnt as it consumed during photosynthesis resulting in a zero net release of CO₂ [Hayes, 1989; Haughton, 1990; Tollefson, 1992]. Also, fossil-fuel sources contain relatively large amounts of sulfur and bonded nitrogen compared to biomass-derived oils. These elements react with oxygen to form hazardous sulfur and nitrogen oxides during combustion and lead to so called "acid rain".

Energy (bioenergy) and chemicals from biomass, on a global basis, can provide some answers to these problems in helping to balance the net production of CO₂ to the atmosphere while meeting future energy and chemical demands on a sustainable basis.

To effectively use wood, especially in the transportation and chemicals industries, it must first be liquefied by pyrolytic [Scott and Piskorz, 1982; ENSYN ENGINEERING ASSOCIATES, Gloucester, Ontario] or high pressure methods [Eager et al., 1982; Boocock et al., 1987] to an oil (wood-oil). However, its direct use is limited by exceptionally high viscosities and non-volatile matter [Eager et al, 1983; Molten

et al., 1987]. Also, the H/C ratios are lower and O/C ratios higher compared to crude-oil from fossil sources. This results in low heating values when used directly. In addition, bio-oils are physically and chemically unstable with time, i.e., there is a continuous variation in the physical and chemical composition with time [Zinkel, 1977; Molten et al., 1978, Leroy et al., 1988]. This factor makes characterization of bio-oils a big problem. Although these undesirable characteristics have been mentioned, neither have detailed studies being undertaken nor attempts made at finding solutions to them. In the first part of this research, attempts were made to characterize the oil obtained from high pressure liquefaction of aspen poplar wood, and an indepth investigation into the instability problem was also carried out. Following these studies, attempts were made to solve the instability problem by using a hydrogen-donor solvent acting as a free radical scavenger.

During the past decade a great deal of attention has been focused on the upgrading of various wood-oils to fuels and chemicals through catalytic conversion methods [Mathews et al., 1985; Soltes and Lin, 1989; Sharma and Bakhshi, 1991]. Efforts have been centred on the production of premium gasoline and important chemicals such as benzene, toluene, xylenes (the BTX compounds) and phenols. The upgrading has been centred on deoxygenation, raising the H/C ratio, and molecular weight reduction.

Two catalytic processing routes are available. One route involves hydrotreating the wood-oil with typical hydrogenating catalysts such as Co-Mo and Ni-Mo [Baker and Elliot, 1987, Soltes and Lin, 1987]. This procedure involves a high pressure operation and most often the catalysts are subject to drastic coking and sometimes poisoning. The second route uses zeolites as catalysts [Chantal et al., 1984, Prasad et al., 1986].

The main advantage of using zeolites over the hydrogenating catalysts resides in the zeolite shape selectivity property. Zeolite shape selectivity has been mentioned [Weisz, 1979, Chen et al., 1989] to be responsible for the restructuring of small molecules and "folding" of large molecules to effective sizes determined by pore size constraints. As such, specific product distributions such as gasoline or kerosene range hydrocarbons have been produced. Furthermore, acid sites can easily be incorporated into the zeolite structure. These acid sites are responsible for cracking, olefin formation, oligomerization, aromatization and isomerization which are reactions essential for hydrocarbon formation. In hydrotreating, catalyst sulfiding is usually required to enhance the activity. The danger associated with this practise is the likelihood of sulfur deposition in addition to metal transfer to the product which can occur in the product. However, with zeolites, catalyst sulfiding is not required for activity enhancement. Medium pore ($\sim 6 \text{ \AA}$) HZSM-5 catalyst is one particular catalyst which has been used widely

in bio-oil processing. It has been used to selectively convert vegetable and wood-derived oils to clean premium transportation fuels and useful chemicals [Chantal et al., 1984, Prasad et al., 1986] and has proved to be effective in converting various oxygenated compounds such as methanol, acetic acid and various aldehydes and ketones to gasoline range hydrocarbons [Chang and Silvestri, 1977; Deroune et al., 1978]. In the light of its proven performance in the conversion of these feeds, HZSM-5 was selected as the catalyst to process the wood-oil with the primary objective of converting it to hydrocarbon-rich products.

As mentioned above, although hydrogenating catalysts are useful for upgrading, they result in rapid catalyst coking and sometimes poisoning, and also require a high pressure operation. On the other hand, as a result of low H/C ratios and instability, direct processing of various wood-oils over HZSM-5 [Chen et al., 1988] also results in a high extent of coking and charring, especially in fixed bed operations. As a result attempts have been made to raise the H/C ratio and improve the oil stability by processing with hydrogen, hydrogen-donor solvents or solvents such as methanol in order to reduce coking and charring [Soltes and Lin, 1987, Sharma and Bakhshi, 1992]. In fossil fuel processing, the use of hydrogen donor solvents such as cyclohexane, decalin and tetralin have been reported to result in the stabilization of the primary products, thus preventing charring or coking and

increasing the yield of upgraded liquids [Bockrath, 1983; Mcmillen et al.; 1987]. Prasad et al. [1986] also reported a reduction in coke formation during the processing of canola oil over HZSM-5 catalyst in the presence of steam compared to the operation without steam. As a result of these developments, upgrading in this research was carried out by mixing the wood-oil with a hydrogen-donor solvent and also carrying out some runs in the presence of steam. The intent was to employ lower operating pressures and prevent the use of high pressure operation often needed during hydrotreatment, raising the H/C ratio, and improving the pumping characteristics of the wood-oil with the objective of limiting coke and char formation.

The few research papers on wood-oil upgrading using zeolites have centred on the use of medium pore HZSM-5 catalyst. Very little information is available on the use or performance of other zeolite catalysts. Also, information on the effect of zeolite characteristics such as pore size, acidity, and shape selectivity on wood-oil upgrading is lacking. In this research, attempts were also made to study these aspects and test the performance of the various zeolite catalysts; large pore H-mordenite and HY, non-acidic silicalite and amorphous silica-alumina in addition to HZSM-5.

Kinetic modeling is an important area in wood-oil upgrading of which very little information is available. The derivation of reaction pathways/mechanisms on one hand and

chemical kinetics (rate of reactions, rate equation etc.) and parameter estimations on the other make up the two vital aspects of kinetic modelling of catalytic processes. The reaction pathways/mechanisms usually provide an understanding into the chemical steps through which the products were obtained. Coupled with rate equations and kinetic parameters, these are used in design equations for sizing of reactors, selection of processing conditions and prediction purposes. Since wood-oils consist of a complex mixture of chemical groups, one vital tool by which chemical steps involved in the processing of these oils are identified is through model compound reactions studies. In this research, model compound reactions were studied and possible reaction pathways for the conversion of the wood-oil were proposed based on these studies. Following this, rate equations and product prediction models were derived. The kinetic parameters were estimated and used in the product prediction models.

Thus, the main objective of this research was to study the viability of catalytically upgrading a wood-derived oil to fuels and useful chemicals. Within this objective, various phases of the research were defined with each phase having set objective(s). These are:

Phase 1.

- a. to produce an oil from aspen poplar wood using the high pressure liquefaction method and to use this oil to investigate:

- i. its distillation characteristics.
- ii. its changes in physical properties, chemical composition and distillation characteristics of the wood-oil with storage time, i.e., stability characteristics.
- iii. investigate the effect of tetralin addition on wood-oil stability and properties.

Phase 2.

- a. Prepare and characterize HZSM-5 catalyst.
- b. Upgrade the wood-oil to fuels and chemicals by mixing with tetralin and processing over HZSM-5 catalyst.
- c. Evaluate the performance of HZSM-5 catalyst in terms of its regeneration.

Phase 3.

- a. Process the wood-oil over HZSM-5 in the presence of steam with the objective of simultaneously producing fuels and chemicals and minimizing coke formation.
- b. Evaluate the performance of HZSM-5 catalyst during upgrading in the presence of steam in terms of its regeneration.

Phase 4.

Upgrade the wood-oil to fuels and chemicals by using different catalysts and also to

- a. evaluate the performance of each catalyst in terms of

yield and selectivity for hydrocarbons in comparison with HZSM-5 catalyst.

b. study the effect of pore size, shape selectivity and acidity of catalyst on yield and selectivity of products.

Phase 5.

With the aid of model compound reaction studies

a. derive reaction pathways for the catalytic conversion of the main chemical groups contained in the wood-oil.

b. propose reaction pathways for the catalytic conversion of the whole wood-oil.

Phase 6.

a. Derive rate expressions and estimate the kinetic parameters.

b. Derive product prediction models based on fixed bed design equation.

c. Using the models, predict the product yields and compare with experimental results.

d. Discriminate between rival models and reaction pathways.

e. Derive hydrocarbon selectivity relations.

2. LITERATURE REVIEW

2.1 Introduction

This chapter presents a review on the catalytic conversion of oils derived from wood (wood-oil) to fuels and chemicals. Emphasis is placed on the preparation and characteristics of wood-oil, experimental methods and factors affecting its upgrading. Catalyst preparation and characteristics, and kinetic modelling of wood upgrading are also described.

Oils from biomass consist of (a) plant or vegetable oils and extracts such as canola, flax, palm, soybean, sunflower, mustard oils, (b) oils produced as by-products of the pulping industry, i.e., tall oil and (c) oils produced from wood through high pressure liquefaction (HPL) and high temperature, low pressure liquefaction (Pyrolysis). This review focuses on oils produced from wood.

2.2 BIOMASS-DERIVED OILS FROM LIQUEFACTION OF WOOD

Wood is the most abundant raw material for the production of bio-oils although urban and agricultural wastes and peat have also been used [Klass and Sen, 1987; Molten et al., 1989]. Wood consists of three basic polymers, cellulose ($C_6H_{10}O_5$), lignin ($C_9H_{11}O_3(OCH_3)_{0.9-1.7}$), and hemicellulose such as xylanes ($C_5H_8O_4$). It is the aromatic nature of lignin which makes wood an important source of useful chemicals. Also present in very small amounts are extractives, minerals and

ash [Sjostrom, 1981; Hall, 1981; Fengel and Weener, 1984; Antal, 1985]. In some woods about 0.1 to 0.25 % nitrogen and up to 0.1 % sulphur have been identified [Tillman, 1978; Hall, 1981]. A typical composition (of aspen poplar wood used in this research) is presented in Table 2.1. In comparison, coal has sulphur contents ranging between 0.6 to 3.1 %.

The liquefaction of wood has been reported [Chornet et al. 1985 a,b] to take place through a complex sequence of structural and chemical changes. These sequence may involve the formation of micellular structures, depolymerization, thermal decomposition leading to new molecular rearrangements through dehydration, decarboxylation, C-O and C-C bond ruptures, hydrogenation and hydrogenolysis. The extent of each reaction depends on the operating conditions, presence of catalyst, solvents and the composition or nature of the original wood material.

Table 2.1
Composition (wt%) of aspen poplar wood (dry basis) [Tillman, 1978, Chornet and Overend, 1982]

| Element | wt% | Building Unit | wt% |
|---------|-------|---------------|------|
| C | 51.64 | @-Cellulose | 50.9 |
| H | 6.29 | Hemicellulose | 21.8 |
| O | 41.45 | Lignin | 18.7 |
| N | 0.0 | Acetyl | 3.5 |
| S | 0.0 | Extractives | 4.45 |
| Ash | 0.65 | Ash | 0.65 |

Three thermochemical methods are available for the conversion of wood into an oil. These are described below.

2.3 Thermochemical Wood Liquefaction

This method involves the direct liquefaction of wood by

1. **pyrolysis at high temperature and atmospheric or low pressures** [Graef et al., 1981; Kaminsky et al., 1982; Boocock et al., 1984; Hichmann et al., 1984; Kallury et al., 1984; Scott and Piskorz, 1984; Radlein, 1987; Reed, 1987; Soltes and Lin, 1987; Diebold and Scahill, 1988; Roy et al., 1989; Graham et al., 1989; Scott et al., 1989].
2. **high pressure liquefaction (HPL)** [Eager et al., 1981, 1983, 1987; Boocock, 1987; White, 1987; Chornet et al., 1988; Boocock et al., 1988].
3. **supercritical extraction** [Jezko and Howard, 1984; Chantal et al., 1984].

Since liquefaction by solvent extraction (3) is usually very expensive and seldom used, emphasis in this review was centred on pyrolysis (1) and HPL (2) methods.

2.3.1 Pyrolysis Method

Pyrolysis oils are produced at high temperatures by vacuum pyrolysis [Roy et al., 1989], entrained flow pyrolysis [Knight et al., 1984; Ayres, 1989], fast pyrolysis [Kaminsky et al., 1982; Reed, 1987; Diebold and Scahill, 1988; Scott et

al., 1989] or ultrapyrolysis [Graham et al., 1989]. Since most of the pyrolysis work has been carried out at atmospheric pressure, emphasis would be placed on this area.

Pyrolysis is the decomposition of feed or biomass by heat in the absence of oxygen. The terms conventional, flash or ultra have been used to describe the pyrolysis in terms of the heating rate [Scott and Piskorz, 1982, 1984, 1988; Reed, 1987].

Pyrolysis has been conducted in the presence of reactive and non-reactive atmospheres [Sundaram et al., 1982; Peters, 1984]. Reactive atmospheres have involved the use of reactive gases, mostly hydrogen (hydropyrolysis) and under pressures of up to 20 MPa. This has been reported [Peters, 1984] to result in valuable liquid and gaseous hydrocarbon products. In non-reactive atmospheres, gases such as helium, nitrogen and argon have been used. In both processes, the pyrolysis of wood yields a hydrogen-enriched gas, a hydrogen-deficient liquid or tar and a carbon-rich solid known as char or coke [Peters, 1984].

Various reactor systems have been used in the pyrolysis of wood to obtain wood-oils. The most popular ones are described below.

At the University of Waterloo, a Rapid Thermal Pyrolysis Reactor (RTP) has been used in the processing of various wood species under flash pyrolysis conditions. This reactor has also been used for various investigations by other workers

[Graham et al., 1984; Freel et al., 1986; Scott et al., 1988]. It consists of a tubular entrained bed reactor and a rapid vertical mixer (a conical vessel) that employs two tangentially opposed heat carrier streams to effect rapid heat transfer and mixing in the order of milliseconds. This set-up has been reported [Scott et al., 1988] to be capable of producing more than 95 wt% liquid at 700 °C and residence times less than 20 ms. A pilot plant which handles feed rates of 100 Kg/h (ENSYN ENGINEERING ASSOCIATES in Gloucester, Ontario, Canada) has been built using the results of this work. This pilot plant employs a heat carrying solid particulate to contact the biomass, giving high heating rates exceeding 10,000 °C/s in a specially designed thermal mixer. The feed and solid heat carrier then passes through a tubular transport reactor in which the pyrolysis reactions experience a controlled residence time. Pyrolysis temperatures ranges between 400 to 1000 °C.

By far the most widely used reactor configuration is the fluidized bed [Scott and Piskorz; 1982, 1984, 1988; Scott et al., 1985; Radlein et al., 1987; Funazukuri et al., 1986]. The advantages of using this system compared to other reactor configurations lies in the possibility of achieving higher mass and heat transfer and reaction rates and near isothermal operation. In addition, it affords continuous operation and controllability. The Waterloo Fast Pyrolysis Process is a very popular apparatus based on the fluidized bed configuration. In

this system, the biomass is fed into the fluidized bed using a variable twin speed screw feeder. It allows recycled product gas to be used as the fluidizing gas. It operates at temperatures of 450-650 °C, residence times of 0.3-1.5 s and N₂ has been used as carrier gas. The yields depend on temperature and heating rates. Optimum yields (total liquids) of 75 wt% of dry feed at a heating rate of 10⁵ °C/s and short residence times have been reported [Scott and Piskorz, 1985].

The Solar Energy Research Institute (Golden Colorado) [Diebold and Scahill, 1987] uses a vortex reactor for the production of pyrolysis oils. The reactor system was designed so that an entrained bed of wood powder and carrier gas enters the vortex reactor at velocities greater than 100 m/s. This reactor has a number of advantages for the fast pyrolysis of biomass including: high heat transfer coefficients which allow the use of moderately low temperatures of the vortex wall to supply the endothermic heat of pyrolysis; separation of the partially pyrolysed feed particles from the char; ability to recycle partially pyrolysed feed; and the ability to use a wide range of particles sizes. About 70 wt% oxygenated vapours based upon mass balances has been achieved with operating temperatures of 480 to 520 °C and recycle loop temperatures of 400 to 450 °C. However, the major problem associated with this method lies in the difficulty encountered in the collection of these vapours.

The entrained flow reactor set-up is another reactor

configuration often used. The two most popular works using this reactor system have been reported by Knight et al., [1984] and Steinberg et al., [1986]. Heating rates from 10^3 to 10^6 °C/s have been reported. The advantages of this type of set-up include the rapid heat-up time, possibility of quenching the reactants and short residence times. The reactors are usually constructed to take the shape of a helix so that high heating rates are achieved but this comes at the expense of capacity. In the reactor system used by Knight et al. [1984], a mixture of wood and carrier gas were forced fed vertically through the reactor under pyrolysis conditions. The products consisted of gases and vapours which were removed from the top of the reactor in a system comprising cyclones, condensers and filters. Up to 51.3 wt% of moisture and ash-free feed at 475 °C was reported. Also, at Georgia Tech Research Corporation, (Atlanta, Georgia), an entrained flow pyrolyzer has been used for the liquefaction of biomass under moderate heating rates and temperatures. The system also contains an upflow reactor and an oil recovery system that allows partial on-stream fractionation of the product. Temperatures from 400 to 550 °C have been used and liquid yields ranging between 31 and 53 wt% have been obtained.

2.3.2 High Pressure Liquefaction (HPL) Method

In the HPL method, a solid wood mass is suspended in a liquid carrier, generally in the presence of a catalyst and contacted at elevated temperatures and under pressure with gaseous reducing agents [Eager et al., 1983; Eager and Pepper, 1987]. HPL has been carried out in batch [Eager et al., 1987, Meier and Faix, 1988], semi-continuous [Eager et al., 1983] or continuous reactors [Appell, 1977; Eager et al., 1984]. Appell [1977] mentioned that water supplied hydrogen for the reaction and also contributed to the hydrolysis of the high molecular weight carbohydrates. It also acts as a solvent and vehicle for the reaction and it lowers the degree of polymerization of some of the high molecular reactive water soluble intermediates.

The reducing gas used is usually carbon monoxide or a mixture of carbon monoxide and hydrogen. These gases are used because of the demonstrated effectiveness in solubilizing coal.

The operating conditions employed have been temperatures between 250 to 400 °C and pressures are determined by the gas produced. Catalysts used include sodium carbonate and hydroxides, carbonates, hydrogen-bicarbonates and formates of alkaline and alkaline-earth metals.

Solvents such as anthracene oil, cresol [Dao et al., 1984, Appel, 1977] and hydrogen-donor solvents such as tetralin [Vasilakos and Austgen, 1985; Araya et al., 1986,] and steam

[Boocock et al., 1987] have also been used in other applications to enhance either the yield or quality of the oil.

At the University of Saskatchewan, an HPL method was developed by Eager et al. [1981] where liquefaction of wood was carried out by mixing it with a solution of sodium carbonate at 360 °C and 35 MPa for 1 h in the presence of CO in an autoclave. Yields of about 35 wt% were obtained. They also observed that all three wood components, i.e., cellulose, hemicellulose and lignin, were converted to bio-oil. About 40 wt% of the oil was non-volatile. The same experimental facility was used in this work and has been described in detail in Chapter 3.

In the University of Toronto, Boocock and co-workers [1983, 1988] carried out various investigations on the high pressure liquefaction of wood. Slurries of powdered wood were fed semi-continuously along with nickel carbonate and hydrogen to a reactor, heated up sufficiently rapid so that the nickel catalyst decomposed to nickel oxide and nickel metal. However, it was suspected that charring of the oil resulted in very low tar yields (up to 25 wt%). The charring was attributed to the long residence times and the absence of a stabilizing component such as nickel metal. As a result, a subsequent work [Boocock, 1983] was designed whereby the powdered wood together with only water was heated rapidly to 350 °C. Oil yields of up to 50 wt% were achieved. On the basis of these

results, a 600 mL cylindrical batch laboratory reactor system was built [Boocock, 1988] with the purpose of studying the liquefaction of commercial-size wood chips in the presence of steam. Poplar or willow woods, in the form of chips, sticks and dowels up to 3 cm diameter, were pyrolysed by steam injection at temperatures from 330 to 350 °C. Acetone-soluble oil yields of 40-50 % were achieved in less than 1 min.

Table 2.2 shows the elemental makeup of a number of bio-oils produced from various sources.

The above mentioned studies have shown that between 31-95 wt% pyrolysis oil and 30-50 wt% HPL oils can be produced by the liquefaction of wood. It has also been shown that the yields and physical condition of these oils depended on factors such as heating rate, feed rates, temperature, pressure, and residence time.

2.4 Characteristics of Wood-oils

Pyrolytic oils contain about 31-37 wt% O compared to 15-20 wt% for HPL oils [Baker and Elliot, 1988]. Pyrolytic oils also contain higher water contents (18-29 wt%) than HPL oils (3-5 wt%). However, pyrolytic oils are far less viscous than HPL oils (apparently due to the water content) and contain low mass organics [Beckman and Oestman, 1985].

Table 2.2
Elemental analysis for some biomass-derived oils (wt %) [Kaliaguine, 1981].

| Element | Pyrolytic Tar from Peat | Oils by conversion of Cellulose | Oil from Manure | Tar from SGE of Red Cedar | Oil from Conversion of Poplar |
|----------------|--|--|----------------------------|--------------------------------------|--|
| C | 64.1 | 72.4 - 81.2 | 78.6 | 60.86 | 79.8 - 76.8 |
| H | 8.2 | 7.0 - 8.4 | 9.5 | 6.22 | 9.2 - 9.5 |
| O | 23.6 | 20.4 - 10.3 | 7.3 | 32.92 | 10.9 - 13.0 |
| N | 3.5 | 0.004 - 0.1 | 4.2 | - | - |
| S | 0.6 | 0.2 - 0.003 | 0.37 | - | - |
| H/C | 1.53 | 1.16 - 1.24 | 1.45 | 1.23 | 1.38 - 1.48 |
| O/C | 0.28 | 0.21 - 0.10 | 0.07 | 0.41 | 0.10 - 0.13 |

The wood-oils have an energy content of $2.3-3.8 \times 10^4$ KJ/Kg compared to $1.8-2.1 \times 10^4$ KJ/Kg for wood [Tillman, 1978; Beckman and Oestman, 1985].

Since wood is structurally complex, the composition of wood-oils is also complex and varies with the method and process conditions. Due to the complex composition, characterization is usually preceded by fractionation since a significant portion is non-volatile. Partial information is usually available from methods such as GC or MS as a major portion of the oil either polymerises or decomposes at the high injector temperatures. Several analytical methods are required to obtain complete analysis of the wood-oils although capillary gas chromatography may yield sufficient information. These analytical methods include elemental analysis, moisture determination by Karl Fisher titration, solids determination, heats of combustion, vacuum distillation, measurements of viscosity, density, mineral content, Conradson carbon, aromaticity by NMR, ash and pour point determination [Eager et al., 1981; Elliot, 1982; Karlsson and Bjornbom, 1982; Soltes and Lin, 1987; Funazukuri et al., 1987; Pakdel, 1987].

Analysis has shown [Poerber and Bauer, 1977; Eager, 1984] that wood-oils consist of a broad molecular mass distribution from 32 to 10,000 and boiling points from 55 to 300 °C. About 30 to 50 % of compounds have molecular masses greater than fuel oils [Appell, 1977, Johnson, 1987]. For instance, Eager et al. [1984] used GPC and HPLC to study the molecular mass

distribution of oils obtained from the HPL of aspen poplar wood by batch and continuous reactors. They observed similar molecular mass distributions profiles, ranging between 100 and 400.

Wood-oils are hydrogen deficient materials. Hydrogen to carbon (H/C) ratios are between 1.0 to 1.5 and oxygen to carbon (O/C) ratios between 0.1 to 2.0 have been reported [Pober and Bauer, 1977; Eager, 1983]. Also, viscosities of wood-oils are generally higher than crude oil from fossil sources, and is a function of the thermal history. Pober and Bauer [1977] studied the viscosity of bark pyrolytic oils. The oils displayed non-Newtonian behaviour, showing hysteresis especially at lower temperatures. The viscosities were also shear dependent. Shear rates and temperatures at which these were carried out were not mentioned in their work. On the other hand, Leroy, et al. [1988] studied the rheological behaviour of sixteen pyrolytic wood-oils in the shear rate range 10^{-1} to 10^3 s⁻¹ and 20 to 80 °C temperature range. It was observed that all the pyrolytic oils exhibited Newtonian behaviour contrary to those observed by Pober and Bauer [1977]. Also, it was found out that these oils displayed a variety of apparent rheological behaviours, ranging from semi-solid to pitch-like and to liquid at room temperature, depending on the preparation procedure and conditions.

One of the most insidious properties of bio-oils in general is their apparent instability; that is, the physical

and chemical properties and composition change with shelf life. Molten et al. [1978] observed a continued polymerization at room temperature of an oil produced from cellulosic wastes. This behaviour was associated with the oxidative coupling of phenols in the bio-oil. Zinkel [1977] also observed the polymerization of tall oil with shelf life and suggested an ionic mechanism involving the unsaturation of the bio-oil components. These unsaturated members are capable of oxidative or thermal polymerization resulting in higher molecular weight oils or coagulation of portions of the oil [Molten et al., 1978; Eager et al., 1981; Davis et al., 1982; Pober and Bauer,; Leroy et al., 1988]. Soltes and Lin [1984] also reported that most pyrolytic oils were unstable and corrosive and quickly forms a solid mass when exposed to air. The corrosive nature has been linked to the acidity of pyrolysis oils (pH between 2.2 and 3.0). This acidity is due to the presence of carboxylic acids such as acetic, formic, glycolic, maleic and acrylic acids.

2.4.1 Chemistry of the Preparation and Chemical Composition of Wood-oils Produced by HPL

Since wood-oil from HPL method was used in this work, it will be worthwhile to explore the chemistry underlying its production, in addition to its physical characteristics and chemical composition.

It has been mentioned earlier on that wood is

structurally and chemically complex. In order to gain insight into the chemistry of the conversion of wood to oils, reactions involving the liquefaction of carbohydrates, cellulose, D-xylose, D-glucose and lignin in aqueous alkaline solutions have often been used as model compounds [Apell, 1977, Eager et al., 1983].

Forsskahl et al., [1976] studied the reaction of D-glucose and D-xylose using 0.63 M NaOH solution. In addition to acidic and aliphatic degradation products, they identified various cyclic enols, phenolic compounds and several furan derivatives. It was postulated from these results that the overall mechanism probably involved a complex combination of fragmentation (creation of C₂ to C₄ fragments) with subsequent recombination and cyclization, partly via base-catalyzed aldol condensation to liquefaction products.

Molton et al., [1978] studied the mechanism of conversion of cellulosic wastes to oils in alkaline solutions. Furans and phenols (including polyfurans and polyphenols) were the major compounds identified. It was suggested that in alkaline solutions, "scissoring" or "peeling" of glucose units from the end of cellulose chains occurs as an initial decomposition reaction. The liberated glucose units then rearrange and cleave by a reverse aldol type reaction, generating saccharinic acids. Further reactions yield furan aldehydes and ketones. In the formation of higher molecular weight oil components from cellulose, as opposed to degradation

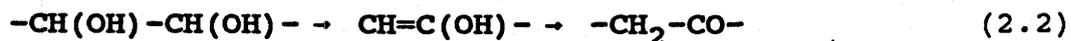
reactions, aldol condensation of single compounds such as ketones and aldehydes was the first major step. Also, it was mentioned [Molton et al., 1978] that the phenols were formed by dehydrogenation or oxidation of cyclohexanone derivatives. The cyclohexanone could be formed from cyclization of terminally unsaturated pentanal and hexanals which are derivatives of simple aldehydes and ketones. The formation of furan derivatives took place through the cyclization of diketones formed from simple aldehydes and ketones using aldol-type condensations.

Appell [1977] also suggested that the mechanism for the conversion of carbohydrates to an oil consisted of the following steps:

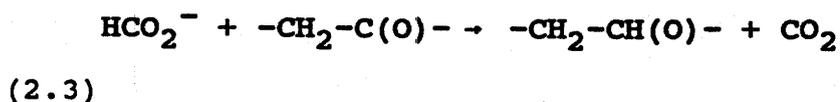
1. Reaction of sodium carbonate and water with CO to yield sodium formate:



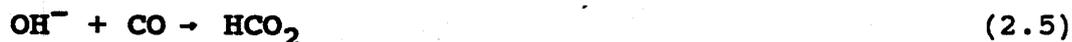
2. Dehydration of vicinal hydroxy groups in a carbohydrate to an enol, followed by isomerization to a ketone:



3. Reduction of the newly formed carbonyl group to the corresponding alcohol with formate ion and water:



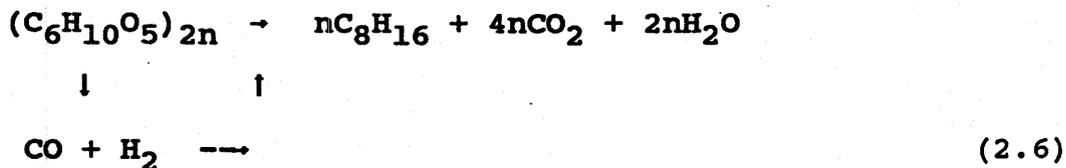
4. The hydroxyl ion, or its equivalent in terms of sodium hydroxide or carbonate, then reacts with additional carbon monoxide to regenerate the formate ion:



There are of course a number of side reactions such as aldol condensation between two carbohydrate molecules which leads to high molecular weight, viscous materials.

Under similar conditions the lignin fraction can also be converted to an oil. In this case Appell [1977] reported the lignin molecule was unstable under these reaction conditions and that it dissociated to lower molecular weight compounds. The CO reduced the carbonyl groups, via the formate (equation 2.4), and eliminated much of the cross-linking and charring normally accompanying the heat treatment of lignin. Also, elimination of condensation and cross-linking reactions by the presence of CO permits stabilization of these lower molecular weight components.

Boocock et al., [1980], produced the following idealized model to describe the liquefaction of cellulose.



In this model, it was suggested that the liquefaction proceeded by the depolymerization of cellulose to yield an organic liquid product represented by C_8H_{16} . Also, it was suggested that all the oxygen was removed as either CO_2 and H_2O .

The preceding information show that the degradation or fragmentation followed by partial recombination are the two major steps involved in the production of oils from wood.

2.4.2 Composition and Characteristics of Aspen Poplar Wood-oil Via High Pressure Liquefaction

Three main analytical approaches have been used to obtain the composition of aspen poplar wood-oil. These include solvent extraction, GC-MS and adsorption chromatography [Davis et al., 1982; Soltes and Lin, 1987]. Usually, a combination of these methods have been employed. In the solvent extraction method various solvents have been used to isolate different portions of the oil. For instance, benzene-hexane has been used to extract non-hydroxylic polar aromatics and oxygen heterocyclics; ether-chloroform for mono-phenols; ethanol-ether for compounds of phenolic nature; and methanol for

polyphenolic compounds [Eager et al., 1981; Davis et al., 1982].

GC and GC-MS methods have been used to identify and determine the concentrations of individual components of the bio-oils [Eager et al., 1981]

In general studies have shown that bio-oils prepared by HPL of aspen poplar consists of non-volatile and volatile fractions [Sharma and Bakhshi, 1991a]. Making up the volatile fraction are compounds such as phenols, cyclic aldehydes and ketones such as alkyl substituted cyclopentanones, acids, cyclic alcohols, polycyclic and long chain alkanes and alkenes, furans, ethers and esters [Graef et al., 1981; Eager et al., 1981; Soltes and Lin, 1987].

By far the most comprehensive work undertaken to study the characteristics of wood-oil produced by the HPL of aspen poplar wood has been by Eager and co-workers [1981, 1983, 1984]. They studied oils obtained from both batch and continuous reactor processes. Their studies encompassed physical characteristics of the oil, water content, elemental analysis and solubility studies. To help identify the chemical composition, they used ^{13}C -NMR to identify the aromatic and unsaturation of the oil, GPC and HPLC to study the molecular weight distribution and a combination of solvent extraction and gas chromatography to identify the individual compounds. The results of these studies are presented in Table 2.3a.

To aid in understanding the mechanism underlying the

conversion of the wood to an oil, they also performed chemical studies on oils derived from cellulose, an isolated aspen polar lignin in addition to aspen poplar wood-oil. Using a combination of extraction and gas chromatography methods, several highly oxygenated products were identified including a mixture of low-molecular weight (C_1 - C_7) aliphatic alcohols, ketones, acids, mono and dinuclear phenols, cycloalkanones, cycloalkanols, and polycyclic and long chain alkanes and alkenes. The major compounds identified are presented in Table 2.3b. Their observations can be summarised as follows: C_1 - C_3 fragments are major constituents which play a major role in the synthetic pathways. In particular, the multi methyl-substituted phenols and cyclopentanones suggested the involvement of these fractions. Carbohydrates and lignins function as precursors for phenolic substances. The origin of cyclopentanones may be predominantly the reactions of the hexose-based cellulose.

Table 2.3a

Characteristics of aspen poplar wood-oil obtained from batch and continuous reactor processes [Eager et al., 1984].

Batch Reactor Process

1. Yield: 33 wt%
2. Description: Pourable at room temperature.
3. Water content: 2.2 wt%
4. Elemental analysis: C, 72%; H, 7%; O, 21%.
5. Heat of combustion: 30×10^6 J/Kg
6. Solubility: Soluble in acetone, methanol and chloroform. Nearly all soluble in benzene and ether.
7. Carbon type by ^{13}C -NMR: 37% aromatic and unsaturated.
8. GPC and HPLC analysis: Mol. mass. distribution, 100-400.
9. Chemical composition: Phenols, naphthols, cycloalkanones, cycloalkanols, polycyclic and long-chain alkanes and alkenes.

Continuous Reactor Process

1. Yield: 40 wt%
2. Description: Viscous at room temperature, pourable at 40°C .
3. Water content: 12.2%
4. Elemental analysis: C, 69%; H, 7%; O, 24%.
5. Heat of combustion: 30×10^6 J/Kg.
6. Solubility: Soluble in acetone and methanol. Partially soluble in chloroform. Sparingly soluble in benzene and ether.
7. Carbon type by ^{13}C -NMR: 50% aromatic and unsaturated.
8. GPC and HPLC analysis: Mol. wt. distribution, 100-400.
9. Chemical composition: Phenols, naphthols, cycloalkanones, cycloalkanols, polycyclic and long-chain alkanes and alkenes, methoxylated phenols and cyclopentanones.

Table 2.3b

Chemical composition of wood-oil from aspen poplar showing main compounds under three main classes [Eager et al., 1983].

Phenolic compounds

Phenol
 o-cresol and 2,6-dimethylphenol
 m- and/or p-cresol
 2-ethylphenol
 2,4-dimethylphenol and/or 2,5-dimethylphenol
 3-ethylphenol and/or 4-ethylphenol and/or 2,3-dimethylphenol

Cyclopentanone (C-P) compounds

2-methyl
 3-methyl C-P
 2,5-dimethyl C-P
 2,3-dimethyl and/or 2,4-dimethyl C-P
 2-ethyl C-P
 2-ethyl-5-methyl C-P
 3-ethyl-2-methyl C-P and/or 4-ethyl-2-methyl C-P
 2-propyl C-P
 2-methyl-5-propyl C-P
 2-butyl C-P

Higher molecular weight

Ethylmethylphenol
 p-isopropylphenol
 p-propylphenol and/or o-propylphenol
 Diethylphenol
 1-Indanol
 3,4-Dimethylbenzaldehyde
 2-Methyl-1-naphthol
 Dimethylnaphthol
 2,5,8-Trimethyl-1-naphthol
 Cycloalkanols
 Cycloalkanones
 Polycyclic and long chain alkanes and alkenes.

2.5 CATALYTIC UPGRADING OF WOOD-OILS TO FUELS AND CHEMICALS

In the previous section the conversion of wood to an oil was described. It was noted that these oils were characterised by high oxygen contents, low hydrogen to carbon (H/C) ratios, high viscosities and high non-volatile matter indicating that for effective utilization in the fuels and chemicals industries they needed to be upgraded. In this section the catalytic upgrading of wood-oils to fuels and chemical feedstocks are described. Part of this section is also devoted to the description of the major processing conditions.

The major purpose of most upgrading work has been the production of volatile hydrocarbon-rich liquid products which could be used as fuel or source of useful chemicals. Efforts have been aimed at enhancing the yields of this fraction through deoxygenation and cracking in order to reduce the non-volatile fraction (lower the molar mass), lower the oxygen content and coke formation, as well as crack multiple-ring components without saturating the aromatic ring [Baker and Elliot, 1988].

2.5.1 Routes of Upgrading

Two main routes have been followed in order to upgrade wood-oils. One route involves conventional hydrotreatment with either H_2 or H_2 -CO mixtures over catalysts related to the classical supported Co-Mo and Ni-MO oxides and the other

involves simultaneous dehydration and decarboxylation over zeolite catalysts, in particular HZSM-5, in the absence of any reducing gas.

2.5.1.1 Conventional Hydrotreatment

Most of the work on hydrotreatment has been carried out using pyrolytic oils as feed. The process details vary in different studies and are described below.

Pyrolysis Oils

A lot of attention has been paid to the upgrading of oils produced by this method. These oils tend to polymerise at high temperatures when subjected to hydrotreatment conditions leading to rapid coking and plugging of reactors. The thermal degradation is probably due to the free radicals generated during preparation [Churin et al., 1990]. Usually, to improve stability, first hydrotreatment is carried out at low temperatures in the presence of hydrogen or hydrogen donor solvents before treatment at higher temperatures. The addition of hydrogen-donor solvents such as decalin and tetralin stabilizes the free radicals. However, only sparse information is available on the stability aspects of these oils or the effect of hydrogen-donor solvents on their stability.

Baker and Elliot [1988] upgraded by hydrogenation, a fast pyrolysis oil produced at Georgia Tech. Upgrading was carried out in a reactor with two temperature stages using Co-Mo/Al₂O₃

catalyst at 13 MPa. The first and second zones were maintained at 274 and 353 °C, respectively. The yield of hydrocarbons was 31 wt% of the oil. They also mentioned rapid catalyst coking as a major problem.

Sheu et al., [1988] upgraded an oil in an autoclave at 400 °C and 6.9 MPa in the presence of hydrogen and tetralin and decalin using 20 different commercial catalysts containing Pt, Pd, Re, Rh, Ru, Ni, Co-Mo and Ni-Mo on various supports. The oil, obtained from Tech-Air Corporation contained nearly 49 wt% non-volatile matter, 43 wt% phenols and 8 wt% aromatics. Upgrading resulted in a decrease in the non-volatile fraction to 24 wt%, phenols to 40 wt% and in aromatics an increase to 22 wt%. Although the exact role of tetralin was not discussed, it may have improved the stability of the wood-oil.

Sheu et al., [1988] also used a trickle bed reactor to upgrade the wood-oil and observed that Pt/Al₂O₃ had the highest activity for oxygen removal. The temperature in the reactor was varied from 350 °C at the inlet to 400 °C at the outlet. This was done so as to prevent the polymerization of the oxygen containing compounds. The upgrading resulted in the cracking of the non-volatile fraction to phenolic components which reacted to hydrocarbons. Sharma and Bakhshi [1991a] also observed similar reactions.

Churin et al., [1990] used a fixed bed reactor loaded with Co-Mo and Ni-Mo catalysts to study the upgrading of

pyrolysis oil. Upgrading was carried out in the presence of hydrogen at 5-12 MPa and 270-400 °C. The oil initially contained 10-20 wt% hydrocarbons and 40 wt% phenols. After upgrading the hydrocarbon fraction increased to 70 wt% while the phenols decreased to 18 wt%. In the presence of tetralin, these fractions increased further to 75 wt% and 20 wt%, respectively. However, the role of tetralin or its recovery was not studied. It was suggested that the phenolic fraction was converted to hydrocarbons, which was also observed by Sheu et al., [1988] and Sharma and Bakhshi [1991a,d]. In this work, it appeared that the phenols were single ringed since low conversions have been reported [Baker and Elliot, 1988] for multiple ringed phenols.

High Pressure Liquefaction Oils

Very little attention has been paid to the upgrading of this oil probably due to the low yields. These wood-oils have been upgraded in the presence of steam or hydrogen. Baker and Elliot [1988] upgraded an oil from poplar wood which had an oxygen content of about 16 wt% over HT-400 Harshaw catalyst. This catalyst contained 3 wt% CoO and 15 wt% MoO on alumina. Upgrading was carried out in a stream of hydrogen at a flowrate of 548-616 L/h, 350-450 °C and 13 MPa. 65 wt% yield of gasoline range hydrocarbons (C₄-C₁₂) was obtained at 400 °C. To obtain these yields, extremely low space velocities and long residence times were used.

However, when an oil prepared by Pittsburgh Energy Research Centre was used, it was found out that the hydrocarbon yield dropped to 29 wt%, apparently due to multiple-ringed phenols. The catalyst deactivated very fast and the results indicated that hydrotreating catalysts have low efficiencies for converting multiple-ringed phenolics.

Boocock et al., [1988] produced a wood-oil by the HPL (20 MPa) of poplar wood in the presence of steam. The yield was about 45 wt%. No upgrading results are available; however, in order to gain a better insight into the chemistry of the upgrading, model compound studies were carried out on compounds such as anisole and phenols. The experiments were carried out in an autoclave using Co-Mo and Ni-Mo catalysts. The highest benzene production from phenol was obtained with sulfided Co-Mo at 350 °C and 1.4 MPa. A significant amount of phenol remained unreacted. With Ni-Mo, the product was mainly cyclohexane. These results showed that phenols and ethers could be deoxygenated using typical hydrodesulphurization catalysts.

The results of these works indicate that up to 75 wt% conversion can be achieved for both HPL and pyrolytic oils by conventional hydrotreatment.

2.5.1.2 Upgrading With HZSM-5 Catalyst

In addition to the conversion of methanol to gasoline [Chang, 1983], it has been shown that a wide variety of heteroorganic compounds can be effectively transformed to hydrocarbons over zeolite catalysts, typically HZSM-5. Complete conversion and between 42-45 % of hydrocarbons in the C₆-C₁₀ range have been produced with alcohols, methanol, t-butanol, 1-heptanol, at 371 °C and atmospheric pressure conditions. The main deoxygenation route was dehydration [Derouane et al., 1978]. With aldehydes and ketones, similar distributions of the hydrocarbon products were obtained, more aromatics being formed with acetone and propanol. Using acetic acid, deoxygenation occurred via decarboxylation and dehydration and the production of hydrocarbons have been reported [Kaeding and Butter, 1975; Chang and Silvestri, 1977; Derouane et al., 1978]. It was this proven performance of HZSM-5 catalyst in converting these oxygenated compounds to hydrocarbon products that formed the basis for its use in the upgrading of wood-oils.

Upgrading using HZSM-5 has been carried out either by using hydrogen or helium as carrier gas or hydrogen donor solvents in order to minimize coking and stabilize the oils. The upgrading of pyrolytic and HPL oils are described in the following sections.

Pyrolysis Oils

At the University of Saskatchewan, Sharma and Bakhshi [1991d] used a fixed bed reactor and tetralin as a hydrogen-donor solvent to upgrade an oil produced by the Waterloo Fast Pyrolysis Process. About 66 wt% conversion of the non-volatile matter, a maximum of 60 wt% organic liquid product and coke fractions between 11 and 17 wt% were obtained.

Chen et al., [1988] achieved 68 wt% conversion of a pyrolytic oil using helium as a carrier gas in a fluidized bed. Upon processing with methanol as a co-feed in a 1:1 weight ratio, the conversion increased to 85 wt%. Also, the methanol resulted in reduced coke formation from 9 to 4 wt%. However, they obtained very low yields of hydrocarbons (6 wt% in the absence of methanol, and 11 wt% with methanol) probably due to the high flow rates (850 mL/min) employed.

Scahill et al., [1988] upgraded the vapours produced by the fast pyrolysis of softwood in a vortex reactor at a steam to wood-oil ratio of 1-1.5 and 450-500 °C. 5-18 wt% liquid hydrocarbon yields containing mainly methylated mono aromatics were obtained.

Milne et al. [1987] investigated the upgrading of wood pyrolytic vapours over HZSM-5 catalyst in a quartz dual-flow reactor with helium carrier gas. 18 wt% hydrocarbon products at 475 °C and 12 wt% coke was obtained. Using methanol as a co-feed, they observed synergistic effects after taking account of the conversion of methanol which resulted in higher

hydrocarbon yields. The effect of WHSV was also studied; however, its effect was not clear.

High Pressure Liquefaction Oils

At the University of Saskatchewan, Sharma and Bakhshi [1991a] upgraded a wood-oil obtained by the method described by Eager et al., [1981] and mixed with tetralin, methanol and steam as co-feeds. Tetralin gave the best results. A maximum of 65 wt% of non-volatile matter (pitch) at 410 °C was obtained with tetralin. The distillate product was 72 wt% at 370 °C and 50 wt% at 410 °C. The phenolic content of the distillate decreased with temperature increase and the amount of aromatic hydrocarbons reached a maximum of 36 wt% at 390 °C. The amount of coke was 11 wt% at 370 °C but increased to 35 wt% at 450 °C.

Also, at the University of Saskatchewan, Mathews et al., [1985] upgraded different fractions of wood-oil over HZSM-5 catalyst using H₂ as carrier gas. The wood-oil was separated into fractions vaporising between 30-150, 150-215, 215-275, and 275-390 °C. The operating temperatures were 350-650 °C. The fraction vaporising up to 150 °C (21 wt% of whole oil) gave the highest conversion to gasoline range hydrocarbons (65 wt%). This represented just a small fraction of the whole oil.

Chantal et al., [1984] investigated the upgrading of an oil (containing 37 wt% oxygen) obtained by gas extraction of aspen poplar wood in a fixed bed reactor operating at 350-450

°C and in a helium flow. 17 wt% gasoline range hydrocarbons, and coke and tar between 10-26 and 10-60 wt% were obtained. Coke and tar formation were found to decrease with the addition of methanol; however, the contribution of methanol was not accounted for. The high tar formation may have resulted from the poor stability of the oil to high temperatures.

From these works the results obtained from upgrading wood-oils with HZSM-5 can be summarised as follows

1. Using a suitable co-feed, such as tetralin, decalin or cyclohexane, higher conversions of wood-oil were achieved accompanied by reduced coking and tar formation. This improvement may be due to the dehydrogenation of tetralin during upgrading. This may have aided in improving the stability of the oil.
2. The performance of HZSM-5 in the conversion of these feeds was comparable to its conversion of methanol.
3. Gasoline range hydrocarbons within the C₅-C₁₀ range were major products. Alkylated benzenes were the main constituents. Octane numbers of these fractions were in excess of 100.
4. Deoxygenation was a major reaction route and proceeded through both decarboxylation and dehydration. Hydroxyl and methoxy groups released oxygen as water. Aryl ethers rejected oxygen in the form of water and carbon monoxide. Carbonyl and formate groups rejected oxygen largely as carbon monoxide and carboxylic groups as carbon dioxide and water [Diebold and

Scahill, 1988].

5. Cracking was another major reaction route.

6. Coke formation was one detrimental aspect of upgrading resulting in catalyst deactivation. Reduction in zeolite aging due to coke formation and yield benefits could be realised in fixed bed operations if low effective hydrogen index (EHI) feeds were co-processed with sufficient amounts of high EHI solvents. Co-processing with methanol resulted in reduced coke formation [Chen et al., 1988].

7. Compounds with $EHI < 1$ which are difficult to upgrade over zeolites in fixed bed operation are possible in fluidized bed reactors under methanol-to-gasoline conditions. Up to about 40 % reduction in coke formation was achieved in fluidized bed operations compared to fixed bed operations [Chen et al., 1988].

2.5.2 Advantages of Using Zeolite Compared to Hydrotreating Catalysts

Although both zeolite and hydrotreating catalysts are able to perform effectively as cracking catalysts, there are a number of advantages when zeolite catalysts are compared with hydrotreating catalysts. These are summarised below.

1. As a result of shape selectivity, zeolite catalysts can provide a definite product distribution which hydrotreating catalysts cannot offer.

2. Zeolites have enhanced resistance to coking due to

sterically hindered transition state selectivity effects [Scott, 1980; Pines, 1981; Weisz, 1979].

3. Hydrodeoxygenation of biomass tars can be achieved when phenolic compounds are in high concentrations. In wood pyrolysis, the liquid products also contain large amounts of low molecular weight organic acids, ketones, aldehydes, furans and phenolic compounds in the methoxy and dimethoxy substituted forms. These mixtures are thermally unstable in typical hydrotreating conditions but can be effectively reacted on zeolite catalysts [Kaliaguine, 1981, 1982].

4. The problem of sulfiding the hydrogenating catalyst in order to increase the activity with the possibility of adding sulfur to the feed are avoided [Kaliaguine, 1981].

5. Water vapour is known to be a poison for hydrotreating catalysts so that eliminating part of the oxygen evolved as CO_2 instead of H_2O might yield an improved stability. Zeolites are known to deoxygenate through both decarboxylation and dehydration [Kaliaguine, 1981, 1982, Chen et al., 1988].

2.5.3 Reaction Conditions

Although upgrading wood-oils is primarily affected by temperature, the oil space velocities, steam to oil ratios, catalysts, use of solvents such as hydrogen donor solvents, time-on-stream and reactor types and configuration do have enough influence to appreciably change the outcome of the results [Chantal et al., 1984; Chen et al., 1988; Sharma and

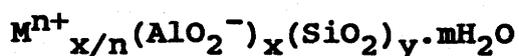
Bakhshi, 1991]. The role of zeolite catalysts, especially HZSM-5 catalyst, hydrogen donor solvent, and steam is often confused since only limited information is available to explain their role during wood-oil upgrading. These three aspects are described below.

2.5.4 HZSM-5 Catalyst

In the following, the applications and the origin of the important physical and catalytic characteristics of HZSM-5 catalyst are described.

2.5.4.1 General Structure of zeolites

Zeolites are porous crystalline aluminosilicates composed of AlO_4 and SiO_4 tetrahedra which form a three-dimensional network linked through the sharing of oxygen atoms. The composition of zeolites can be represented by the empirical formula expressed as



(2.7)

where M is a cation with charge $n+$, m is the number of water molecules of crystallization, $x+y$ is the number of tetrahedra in the unit cell [Campbell, 1983].

To form cavities, the basic tetrahedra units combine to form square ($x4$) and hexagonal ($x6$) plane faces, which combine further to form sodalite cages and hexagonal prisms or cubes [Campbell, 1983; Szostak, 1989] as shown in Figure 2.1.

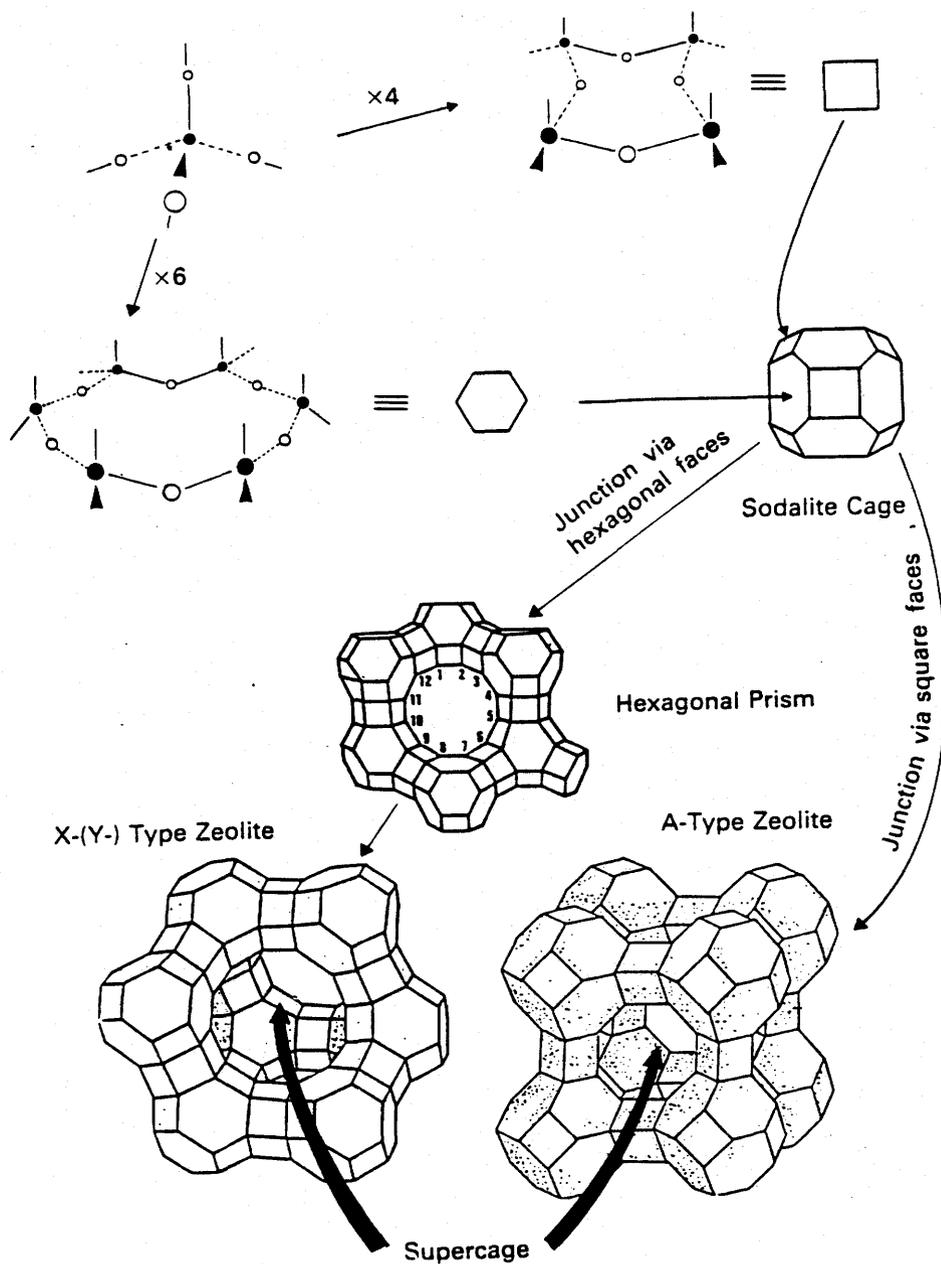


Figure 2.1. The basic structural units and the modes of their combination in A-, X-, and Y-type zeolites. Si or Al atoms are denoted by ●; oxygen atoms are denoted by O [Campbell, 1983].

Structure of ZSM-5

The ZSM-5 zeolite basic unit is composed of 5 silica/alumina tetrahedra linked into a pentagon (secondary building unit) (Figure 2.2). To form the ZSM-5 structure, first, a basic building unit formed by the pentagons linking through the sharing of oxygen atoms (Figure 2.2a) is created. These units join together to form a building block (extended chain building unit) (Figure 2.2b) which also join to form a sheet building unit. The sheet structure repeats in the third dimension, so creating linear channels of slightly elliptical form. These three dimensional structures are characterised by aperture dimensions of 0.56 x 0.54 nm. Further channels occur in the other two dimensions, one sinusoidal with aperture dimensions of 0.55 x 0.51, and the other a tortuous system created by the overlapping of the first two. The complete channel structure is shown in Figure 2.3 and Figure 2.4 shows the pore sizes created by these structures [Campbell, 1983; Szostak, 1989; Dyer, 1988].

2.5.5 Zeolite Shape Selectivity and Acidity

The reactivity and selectivity of zeolites are determined and controlled by the framework structure of the zeolite and presence of acid sites. The selectivity of zeolites has been described by the term shape selectivity and functions by either reactant, product or transition-state selectivity effects [Dyer, 1988; Szostak, 1989]. The acidity has been

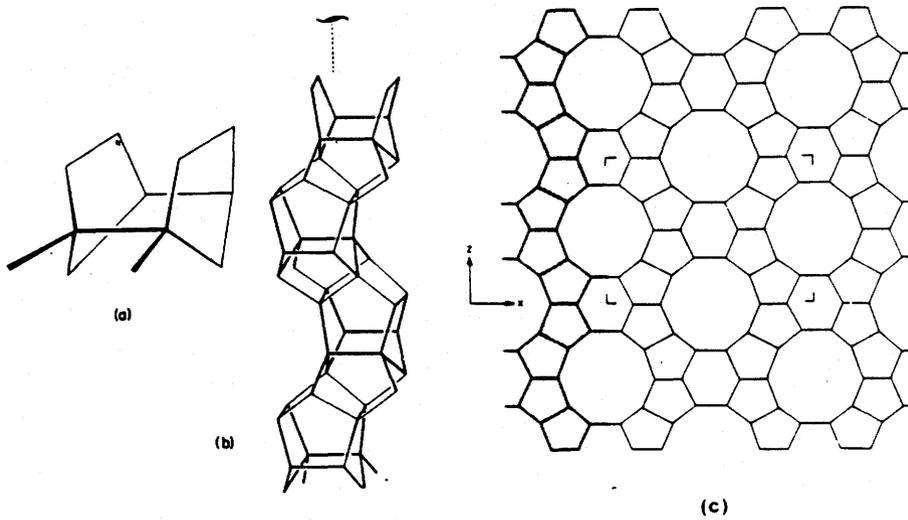


Figure 2.2. Secondary building blocks (a) chain-type building block, (b) layer structure, (c) (with the chain of (b) shaded), indicating how the structure of HZSM-5 is built up [Campbell, 1983].

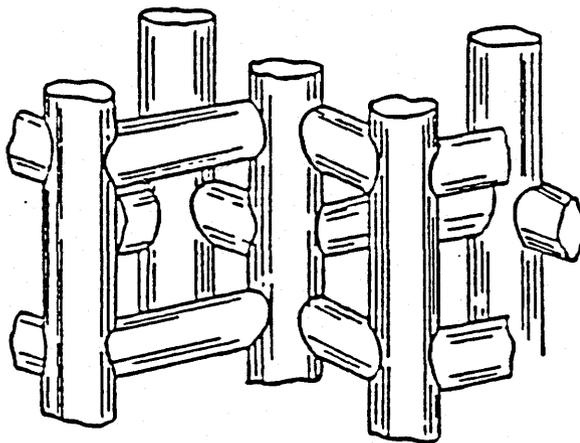


Figure 2.3. ZSM-5 channel system [Dyer, 1988].

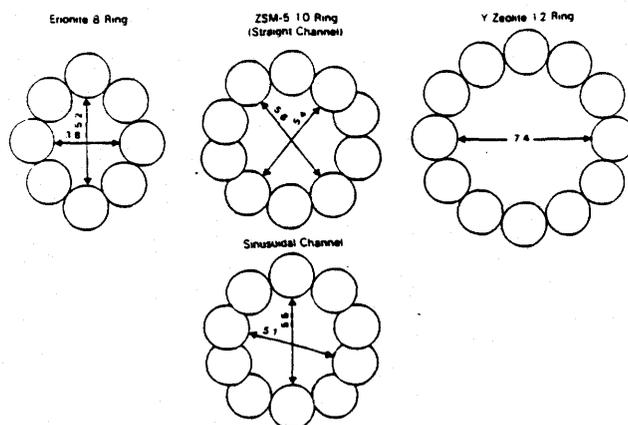


Figure 2.4. Examples of the three types of pore openings in the zeolite molecular sieves showing Erionite with 8 ring pore openings, ZSM-5 with two 10 ring systems differing in the shape of the opening, and type Y zeolite, a 12 ring pore system [Szoztak, 1989].

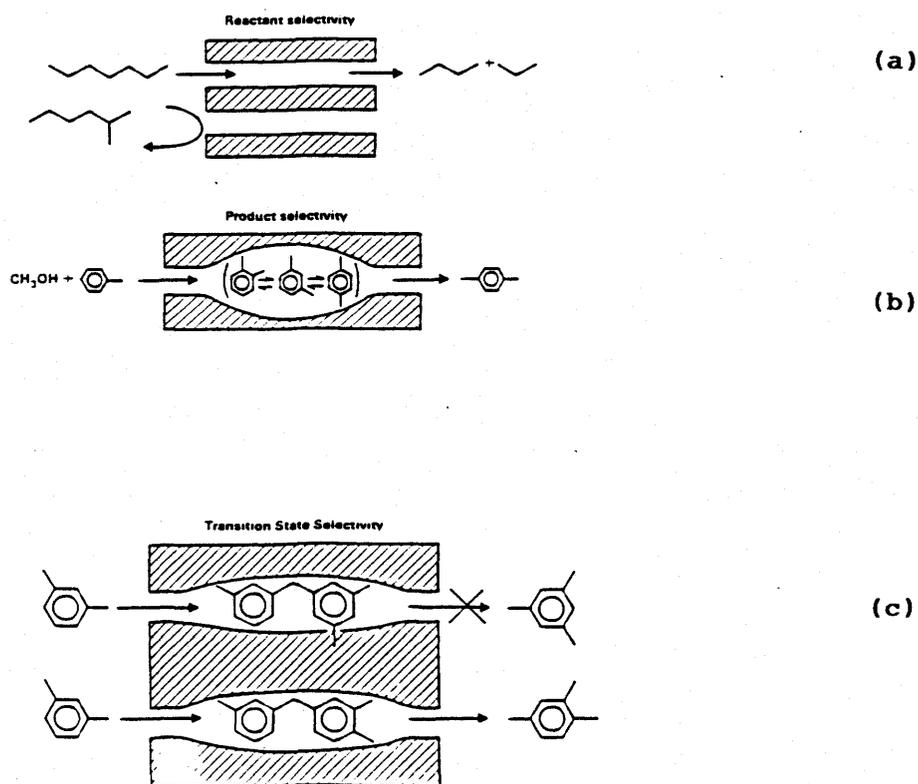


Figure 2.5. Reactant (a), product (b) and transition state (c) selectivities in zeolite channels [Dyer, 1988].

described by the Bronsted and Lewis acid models [Dyer, 1988; Szostak, 1989]. In the following, these aspects of zeolites are described.

Reactant Shape Selectivity

This occurs when control of the reaction process is based upon the exclusion of a particular reactant and the allowance of another reactant to diffuse past the pore mouth. This type of selectivity is depicted in Figure 2.5a. It arises from the limited diffusivity of some of the reactants which cannot effectively enter and diffuse inside the pores as a result of its size or orientation [Dyer, 1988; Szostak, 1989].

Product Shape Selectivity

This occurs when the diffusing product molecules are so slow or cannot escape rapidly enough from the pores, that they engage in secondary reactions. This is essentially a function of the rates of diffusion of products away from the active sites within the crystal. The production of para-isomer rather than ortho or meta-xylene in the alkylation of toluene over HZSM-5 is an example. The diffusion of p-xylene is far greater than that of o- or m-xylene [Dyer, 1988; Szostak, 1989]. This type of selectivity is depicted in Figure 2.5b.

Transition-state Shape Selectivity

This is a kinetic effect arising from the local environment around the active site where the rate constant for a certain reaction mechanism is reduced if the necessary transition state within the pore is too bulky to be accommodated. That is, the volume available around the active site in the zeolite framework is such as would preclude the formation of bulky intermediates [Dyer, 1988; Szostak, 1989]. This is illustrated in Figure 2.5c.

Zeolite Acidity

In petrochemical reactions, zeolite catalysts serve important roles in reactions such as cracking, isomerization, polymerization and disproportionation [Scott, 1980; Chen et al., 1989]. These reactions have been postulated to proceed through intermediate compounds called carbenium ions which are created on the surface of these zeolites [Wojciechowski and Corma, 1986; Chen et al., 1989] through interaction of reactant molecules with active acid sites. Zeolites then act as "solid acids" which are capable of converting the adsorbed molecule into various forms. This is accomplished by either transforming a proton from the solid acid to the adsorbed molecule (Bronsted acid site) or by transferring electron pairs from the adsorbed molecule to the solid surface (Lewis acid site). This zeolite acidity arises from the imbalance in charge between silicon and aluminium atoms within the

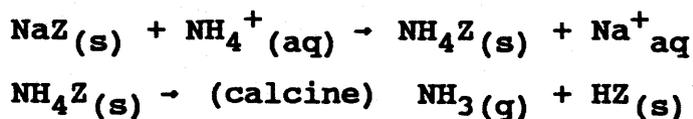
framework so that each aluminium atom is capable of inducing a potential active acid site. The origin and characteristics of these sites are described below.

Bronsted Acidity

This is a proton-donor acidity which occurs when the cations balancing the framework anionic charge are protons (H^+). This form contains hydroxyls which are protons associated with negatively charged framework oxygens linked into alumina tetrahedra [Michiels and De Herdt, 1987; Dyer, 1988]. Bronsted acid sites are depicted in Figure 2.6a.

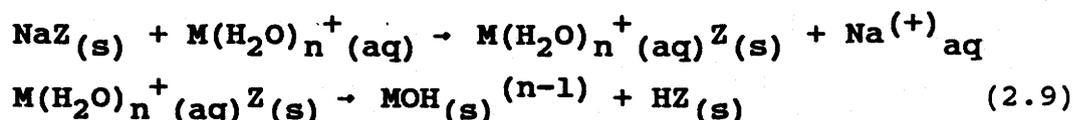
Various methods are used for the production of Bronsted acid sites, or the creation of "hydroxyls" within the zeolite pore. These include:

1. Ammonium ion exchange



(2.8)

2. Polyvalent ion exchange



3. Direct exchange with mineral acids. These are accomplished in mainly high-silica zeolites such as ZSM-5.

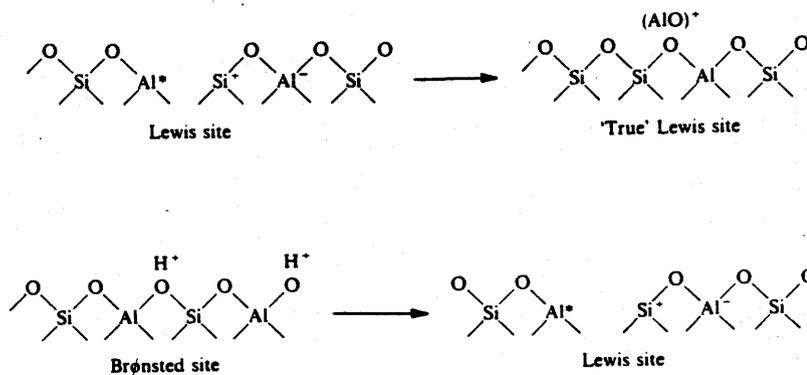


Figure 2.6. Brønsted and Lewis acid sites in zeolites [Dyer, 1988].

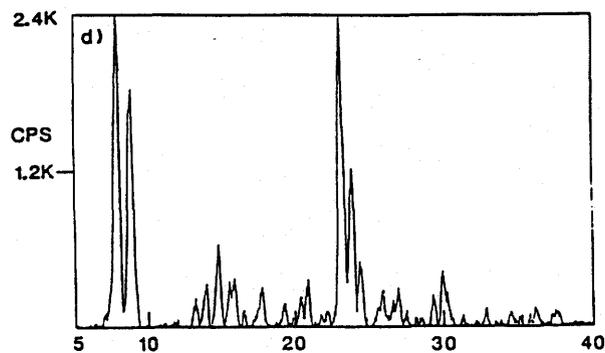


Figure 2.7. X-ray powder diffraction of a pure single crystalline ZSM-5 [Szoztak, 1989].

Bronsted acid sites are believed to be responsible for the high activity of most acid zeolites [Cusumano et al., 1978; Chen et al., 1989]. However, a complete understanding of the entire phenomenon of Bronsted acid activity on the surface is still not well understood.

Lewis Acidity

The role of Lewis acid sites is not very well understood. However, the initial cracking of high molecular weight feeds has been suggested to occur on Lewis acid sites [Prasad et al., 1986].

Lewis acid sites are understood to be generated from the dehydration of Bronsted acid sites. Protons are noted to be very mobile at temperatures beyond 200 °C, and at 500 °C they are lost as water with the formation of Lewis acid sites [Dyer, 1988]. This is depicted in Figure 2.6b.

2.5.6 Synthesis of Zeolite Catalysts

The synthesis of zeolites start with crystallization from an inhomogeneous gel created from a silica source and an alumina source, combined with water under high pH conditions generated by OH⁻ ion concentrations [Michiels and De Herdt, 1987; Dyer, 1988]. Control of the SiO₂:Al₂O₃ ratio in this gel determines the final framework composition of the product. For most laboratory synthesis the source of aluminium is metal aluminates such as sodium aluminate. For silicon, widely used

sources are soluble silicates and their hydrates such as sodium metasilicate pentahydrate and silica sols. Alkali metals and alkaline earth metals are usually used as the source of cations. The correct combination of concentration, temperature, pressure and time are critical to the formation of the exact zeolite structure required.

2.5.7 Synthesis of HZSM-5

The synthesis mixture is typically prepared by combining sodium aluminate, sodium silicate, tetrapropylammonium (TPA) bromide, sodium hydroxide and sodium chloride. The TPA bromide being added to provide a templating role during nucleation and crystallization. Following crystallization, the dried product is calcined between 450 to 550 °C to remove the TPA ions occluded in the structure [Cusumano, 1978; Scott, 1980]. This produces Na-ZSM-5. Ion exchange with the exact concentration of HCl solution results in the production of HZSM-5.

2.5.8. Characterization of Zeolites

A number of methods are used to identify and characterize zeolite catalysts. The two main areas of characterization have been zeolite structure and acidity. X-ray diffraction analysis and spectroscopic methods such as scanning electron microscopy (SEM) have been used in structure characterization, whereas infrared spectroscopy (IR) and/or temperature programmed adsorption and desorption studies (TPA/D), and catalytic tests

have been used for acidity characterization [Topsoe et al., 1981, Jamin et al., 1988; Szostak, 1989].

In the following, structure characterization by XRD and acidity characterization by IR, TPD and catalytic tests are discussed.

2.5.9 Structure Characterization by X-ray Powder Diffraction

This method is used to fingerprint zeolites. In this method, x-ray irradiation of zeolite powders is carried out providing a scattering from the regular array of atoms or ions within the structure. This reflects the framework and non-framework symmetry of the composition of each zeolite to produce a diagnostic fingerprint of 2d spacing according to the Bragg equation:

$$n\lambda = 2d\sin\theta \quad (2.10)$$

[Dyer, 1988; Szostak, 1989]. No two material will have identical diffraction patterns.

Appendix A presents x-ray diffraction data for various zeolites including HZSM-5 that appear in literature and a typical pattern for ZSM-5 catalyst is shown in Figure 2.7.

2.5.10. Characterization of Acid Sites

Acid site characterization involves methods that would provide information on the nature, number, strength and

location of active sites. IR, TPA/D, combination of TPA/D and IR have been used extensively for this purpose. These methods are described below.

Infrared (IR) Spectroscopy

This is used for both acid site identification through structural information and is usually carried out by observing and locating bands absorbed by a sample in the infrared region.

For acid site identification, both quantitative and qualitative measurement of hydroxyl (OH) groups on the surface of the catalyst are made. Both Bronsted and Lewis acids can be identified by this method. For instance, IR have shown that ZSM-5 has two stretching bands, one at a wavelength 3605 cm^{-1} and identified as Al-O-(H)-Si bridge, and the other at 3720 cm^{-1} identified as silanol SiOH groups [Szostak, 1989]. A typical IR band for HZSM-5 catalyst is shown in Figure 2.8.

Temperature Programmed Adsorption and Desorption

This method involves the quantitative measurement of the amount of gaseous base adsorbed on the surface at varying temperatures. Ammonia and pyridine have been used as the main basic probe molecules [Topsoe, 1981; Szostak, 1989]. For instance, pyridine adsorption coupled with IR spectroscopy have been used for detecting Bronsted and Lewis acidity on ZSM-5 catalyst. A stretching vibration at ca. 1540 cm^{-1} is

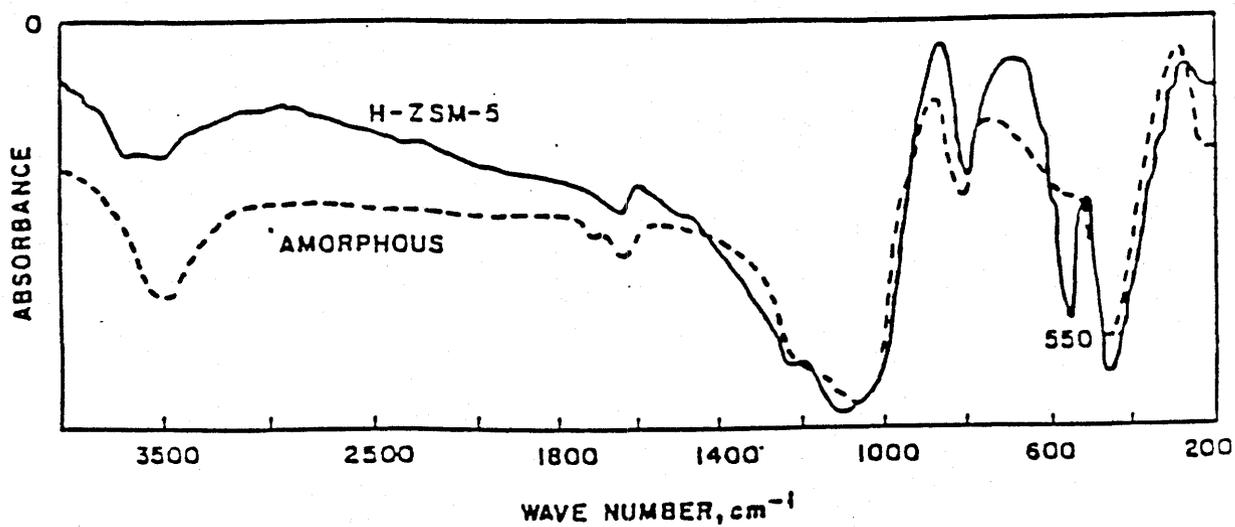


Figure 2.8. IR spectra of HZSM-5 and amorphous silica-alumina [Esponzoza et al., 1983].

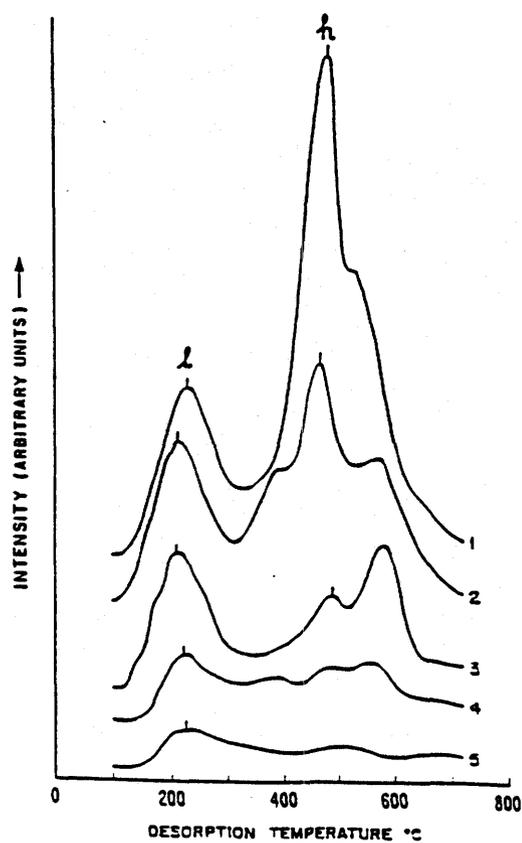


Figure 2.9. TPD of ammonia trace for HZSM-5 [Prasad et al., 1986].

attributed to the pyridine ion (Bronsted-bound pyridine), whereas a stretching vibration at ca. 1450 cm^{-1} is attributed to coordinated pyridine (Lewis-bound). A combination at ca 1485 cm^{-1} is due to both Lewis and Bronsted-bound pyridine stretching vibrations [Jamin et al., 1988]. A typical TPD of ammonia for HZSM-5 is shown in Figure 2.9. The temperature at which ammonia desorbs can be correlated with particular acid sites. The spectra indicate two distinctly different states of chemisorbed ammonia occurring at $227\text{ }^{\circ}\text{C}$ and $460\text{ }^{\circ}\text{C}$. The peaks, l, is said to correspond to Lewis acid sites and h to Bronsted acid sites.

Other methods uses catalytic probe reactions such as the cracking of n-hexane (alpha test), n-butane and n-decane have been used in studying acidity.

Also, for general characterizations, test reactions have been performed where a comparison is made between the product distributions obtained with the catalyst and those reported in the literature. For instance, the product distribution of methanol has been used for identifying HZSM-5 [Chang, 1983].

2.5.11 Hydrogen Donor Solvents

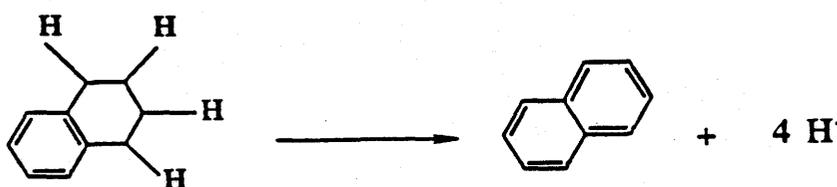
In this section the nature, applications and implications of processing with H-donor solvents are presented.

Also termed liquefaction "solvents", these are reactive solvents which act on the hydrogen donor principle; i.e., they are capable of taking on hydrogen very easily and can also

readily give up hydrogen to form their respective condensed aromatic hydrocarbons [Grainger, 1981; Bockrath, 1983]. Examples of such solvents are tetralin (1,2,3,4-tetrahydronaphthalene), indoline, 1,2,3,4-tetrahydroquinoline.

Hydrogen donor solvents have been used extensively in the processing of coal. In coal liquefaction this has often resulted in the stabilization of reactive fragments such as free-radicals and in dissolution of such fragments during the initial stages of liquefaction. In the upgrading of coal liquids, hydrogen donor solvents have been used to effect hydrogenation, removal of heteroatoms and reduction in molecular weight [Kang, 1976; Bockrath, 1983; Vasilakos and Austgen, 1985].

In these reactions, the dehydrogenation of tetralin has been observed to proceed by the following reaction route:



Hydrogen donor Solvents in Biomass Liquefaction and Bio-oil Processing

The original use of Hydrogen donor solvents was in the processing of coal. However, of late these solvents have gained much importance in the biomass liquefaction and

upgrading of bio-oils [Vasilakos and Austgen, 1985; Kocker and Nelte, 1988; Sharma and Bakhshi, 1991a,c].

In biomass liquefaction, hydrogen donor solvents have been used in the dissolution of peat and wood. Hornell et al., [1988] used tetralin in the liquefaction of wood, peat and coal and found out that peat and wood were more reactive than coal in thermal dissolution in tetralin. Also, Vasilakos and Austgen [1985], using tetralin as hydrogen donor solvent in the catalytic liquefaction of biomass, achieved an enhanced reduction in the oxygen content.

The coking and charring of wood-oils in fixed bed operation as a result of low H/C ratios have been mentioned in the previous sections. Various attempts have been made to process bio-oils with hydrogen donor solvents [Soltes and Lin, 1987; Sharma and Bakhshi, 1991a,c] with the aim of reducing the coke formation by improving the stability of the oil to temperature effects. In addition, the solvation property of hydrogen donor solvents enhances the effective transport of these feeds, thus preventing pore blockage which is a problem with feeding of bio-oils into reactors. Increased yields of hydrocarbons have also been observed [Vasilakos and Austgen, 1985]. For instance, Sharma and Bakhshi [1991a] processed tall oil in a mixture with tetralin and achieved up to 91 % conversion and a product containing about 50 % C₆ to C₉ hydrocarbons. On the other hand, conversions of up to 70 % (containing 39 % C₆ to C₉ hydrocarbons) were obtained with

methanol. Also, Churin et al. [1988] achieved substantial increases in hydrodeoxygenation and hydrodenitrogenation when pyrolytic oils were co-processed with tetralin.

The advantages that can be achieved from using these solvents include diminished decarboxylation, enhanced hydrocarbon yields, reduced coke formation, improved overall conversion and enhanced flow properties. Also, hydrogen donor solvent affects the hydrogen balance when used in upgrading. Starting with a material with a high oxygen content, dehydration as a sole means of oxygen removal will yield a product with a very low H/C ratio, much lower than fuel requirements. Some of the products may of course lose CO₂ or CO in the zeolite structure but much of the alcohol, aldehydes, ketones and phenols will be deoxygenated via water formation. The addition of a hydrogen donor solvent helps to alleviate this problem [Kaliaguine, 1982].

Hydrogen donor Solvents Versus Hydrogen

Most of the processing of bio-oils by hydrotreatment have been carried in the presence of hydrogen. These processes employ high pressures. The main advantage of using hydrogen donor solvents over hydrogen is the much lower operating pressures that can be employed in its use. In addition, hydrogen donor solvents have better effectiveness in stabilizing the primary thermal decomposition products, thus preventing charring and coking in upgrading work [Vasilakos

and Austgen, 1985] with resulting higher yields for upgraded liquids than hydrogen.

Tetralin as Hydrogen Donor Solvent

The selection of a solvent can have a profound effect on the yield of liquids products. A number of compounds are available as hydrogen donor solvents as long as they contain mobile carbon-hydrogen bonds [Vasilakos and Austgen, 1985]. A good solvent readily dehydrogenates and enhances solvation capabilities [Kang, 1976; Grainger and Gibson, 1981; Bockrath, 1983]. In addition, it possesses acceptable physical properties such as reasonable viscosity. High liquefaction yields and reduction in char and coke formation are also expected of a good hydrogen donor solvent. Tetralin (1,2,3,4-tetrahydronaphthalene) compared with similar solvents has proven to possess these exceptional properties in both coal and biomass processing to liquid products.

2.5.12 Co-feeding Steam

Only a few workers have carried out upgrading of bio-oils or similar compounds in the presence of steam. The main objective in situations where this has been done was reduction in coke formation and prolonging of catalyst life. Prasad et al. [1986] showed that the presence of steam in the upgrading of canola oil to hydrocarbons resulted in improved catalyst life. Also, Oudejans et al. [1982] observed improved catalyst

life when they investigated the conversion of ethanol to hydrocarbons in the presence of water. Other observations during such co-feeding include higher C₂-C₅ olefin selectivity and changes in the rates of reactions such as oligomerization and dewaxing [Garwood et al., 1979a, 1979b].

The role of water or steam molecules in these processes is not very well understood. However, two plausible explanations have been provided. Ison and Gorte [1984] observed that water preferentially interacted with the Bronsted acid sites in the zeolites and so postulated that the changes in the reaction pattern may be due to the interaction between steam and the adsorbed intermediates rather than the presence of hydronium ions. Prasad et al. [1986] on the other hand explains these observations on the basis of changes in the rates of the acid catalyzed reactions such as olefin formation, cyclization, isomerization and hydrogen transfer rather than on the changes in the acid strength distribution of the catalyst.

2.6 KINETIC MODELING OF WOOD-OIL UPGRADING

The importance of kinetic modelling in catalytic processes has already been mentioned in chapter 1. In this section, a detailed description is provided on the modelling of the catalytic conversion of wood-oil. As in all catalytic processes, four operations are carried out during modelling. These include the development of reaction pathway(s) consistent with observed product distributions, development of an algebraic rate-law consistent with experimental observations (Chemical kinetics), estimation of rate-law parameters from experimental data and derivation or design of a catalytic reactor model to achieve specified conversions and yields.

These areas are described below. Also, modelling by derivation of hydrocarbon selectivity relations are described.

2.6.1 Reaction Pathways/Mechanisms

Reaction mechanism is the term used to describe all the individual collisional or other elementary processes involving molecules, atoms, radicals and ions that takes place simultaneously or consecutively to produce the overall reaction [Espenson, 1981; Moore and Pearson, 1981]. The reaction pathway is usually used for processes that involve complex feeds and where the individual steps are usually a lumping together of a number of elementary steps [Westerterp et al., 1984].

Usually several reaction mechanisms/pathways can be used to explain the same experimental result so that further experimentation is carried out to eliminate the less likely ones. In bio-oil processing, this is usually done by using model compound reactions [Chantal et al., 1985; Dao et al., 1987; Evans and Milne, 1987]. Isolating parts of the reaction pathway/mechanism and performing separate experiments on these paths as suggested by Levenspiel [1971] and Swinbourne [1971] for the treatment of complex reaction networks are yet to be adopted in wood-oil processing. These two methods are discussed below.

2.6.1.1 Model Compound Reactions

Compounds which can be used as representatives of a particular reaction, chemical or functional group and the reactivity behaviour of which would provide vital information on the overall or parts of the reaction are termed model compounds. Reactions of model compounds are used as tools in identifying the controlling reactions of a complex reaction process and determining synergistic effects among reactants and products. Also, they are used in identifying the chemical species or groups responsible for particular chemical behaviours such as deactivation by coking. Furthermore, by use of model compound reactions, process conditions that should be employed to enhance or inhibit particular reactions can be determined. In catalytic processes where different models can

be used to predict the same product distribution, model compound studies have been an effective tool in discriminating between rival reaction models. Model compound reactions have also been used as aids in studying certain reaction aspects such as deoxygenation, coking, cracking and hydrocarbon formation [Chantal et al., 1985; Doa et al, 1987; Evans and Milne, 1987]. Some of the studies involving model compounds from bio-oils are presented below.

Dao et al. [1988] investigated the reactions of model compounds of biomass-pyrolysis oils over HZSM-5 in a fixed bed reactor. The compounds studied included cyclopentanone, cyclopentenone, furfural, glycol, glucose and fructose. They observed that cyclopentanone can be deoxygenated with high hydrocarbon yields at 400 °C. Addition of methanol (EHI = 2) to cyclopentenone to raise the H/C ratio permitted deoxygenation. Furfural and glycol produced pyrolytic products of various volatility. The volatile fraction was deoxygenated to produce hydrocarbons, while the non-volatile fraction remained on the catalyst bed causing deactivation of the zeolite and enhanced the tar formation. Glucose and fructose underwent thermal reactions which produced significant amounts of tar and small amounts of volatile products. The volatile fraction was deoxygenated to hydrocarbons. It was concluded from their work that for compounds with low EHI, conversion to hydrocarbons was small since the main deoxygenation reaction was the elimination of H₂O which was dependent on H₂

availability. Tar and coke yields were high with low EHI compounds. However, when the EHI was raised by addition of methanol, the tar and coke formation decreased and hydrocarbon yields increased.

Chantal et al. [1985] investigated the conversion over HZSM-5 of several light phenolic compounds most of which were observed as pyrolysis products of lignin. The compounds encompassed phenol, o-, m- and p-cresols, dimethylphenol, eugenol, iso-eugenol, guaiacol, anisole, diphenylether and 2,6-dimethoxyphenol. They proposed mechanisms in which Bronsted acid sites and carbenium ions interacted with ether intermediates, namely diphenylether and anisole to produce various products.

Boocock et al. [1989] investigated the catalytic hydrodeoxygenation (HDO) of wood-oil model compounds involving phenol, anisole and guaiacol over conventional hydrotreating catalysts. Conversion of phenol was maximum 96% at 375 °C over sulfided catalyst. 74 wt% and 16 wt% yields of benzene and cyclohexane, respectively, were obtained. HDO of anisole yielded mainly phenolics, aromatics and cycloparaffins. Again benzene was the major product. HDO of guaiacol yielded a maximum of 59 wt% aromatics and 21 wt% cycloparaffins at 375 °C. It was shown that these compounds can be converted over conventional HDO catalysts such as $\text{MoO}_3/\text{NiO}/\text{Al}_2\text{O}_3$ and $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$ in either the oxidised or sulfided forms to products rich in aromatics, cycloparaffins or phenols.

2.6.1.2 Method of Isolation

This method, also called the partial analysis of rate data, involves separating the reaction rate expression into various parts and performing kinetic runs using components involved in these parts only [Levenspiel, 1971]. In so doing the kinetic parameters of the various parts of a rate model could be determined. A similar method, the competition experiments method, is used to study the reactivity of intermediates [Swinbourne, 1971].

2.6.1.3 Reaction Pathways Reported on Wood-oil Upgrading

Unlike gas oil processing, very scarce information is available on the mechanism or reaction pathways for wood-oil upgrading. A typical reaction pathway for the upgrading of gas oils over zeolites is shown in Figure 2.10 [Wojciechowski and Corma, 1986]. It postulates that the first step in the production of gasoline involves the formation of unstable gasoline molecules through processes that includes mainly cracking, hydrogenation and oligomerizations. Saturates, olefins and naphthenes are formed in this stage. The gasoline olefins and naphthenes are stabilized by converting them into thermodynamically stable aromatics and paraffins.

Using HZSM-5, Sharma and Bakhshi [1991a,d] proposed a reaction scheme for the upgrading of a HPL oil. The reaction scheme is reproduced in Figure 2.11. According to this scheme, the components of the non-volatile pitch are first cracked to

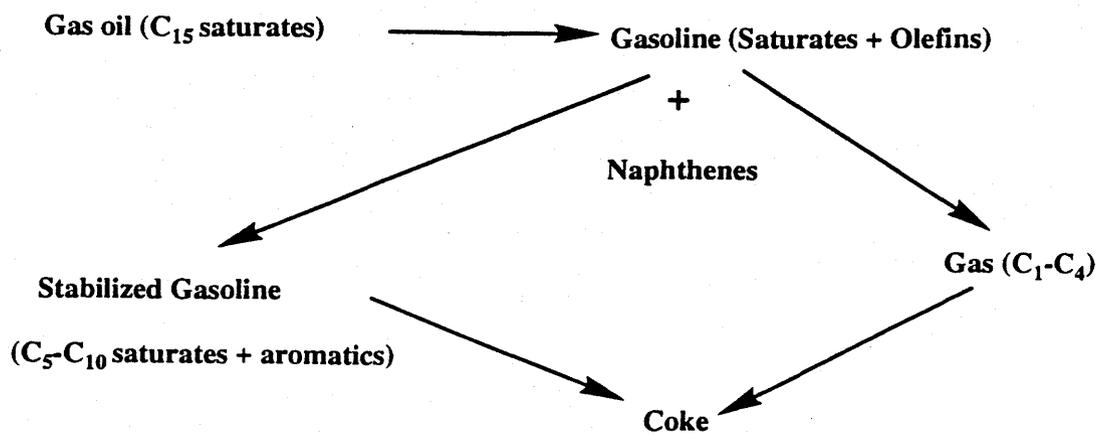


Figure 2.10 Typical reaction pathway for gas oil processing over zeolites catalysts [Wojciekowski and Corma, 1986].

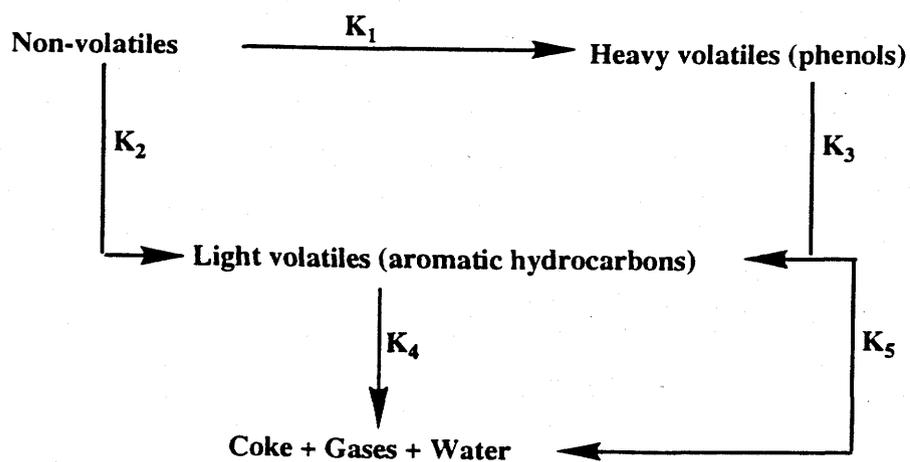


Figure 2.11 Reaction scheme for upgrading HPL oil [Sharma and Bakhshi, 1991a].

heavier volatile phenols and lighter aromatic hydrocarbons. Some of these two fractions react to form coke, water and light gases.

In the conversion of a wood-oil over classical hydrotreating catalysts, Baker and Elliot [1988] proposed 3 typical model structures required to produce liquid hydrocarbon fuels. The model structures are shown in Figure 2.12. They observed that deoxygenation, cracking and hydrogenation of the high molecular weight components are the rate limiting steps in upgrading wood-oils so that catalyst development should be directed at these. Also, they postulated that where the wood-oil is single ring dominated (structures 1 and 2), and where gasoline boiling point range material is the primary product, Co-Mo catalysts are preferred over Ni-Mo because they retain the aromatic character and antiknock properties of the product. Ni-Mo produce lower octane rating products. Deoxygenation and/or hydrogenation were the major reaction routes. For double ringed dominated oils, (structure 3) a more active hydrogenation catalyst such as Ni-Mo may be beneficial. Deoxygenation, hydrogenation, cracking and secondary cracking may be required to obtain the final hydrocarbon product. It was also mentioned that adding the cracking properties of a zeolite can be advantageous.

Also, Soltes and Lin [1987] performed kinetic modelling studies for hydroprocessing of pyrolysis oil in a trickle bed reactor, and proposed the lumped kinetic scheme shown in

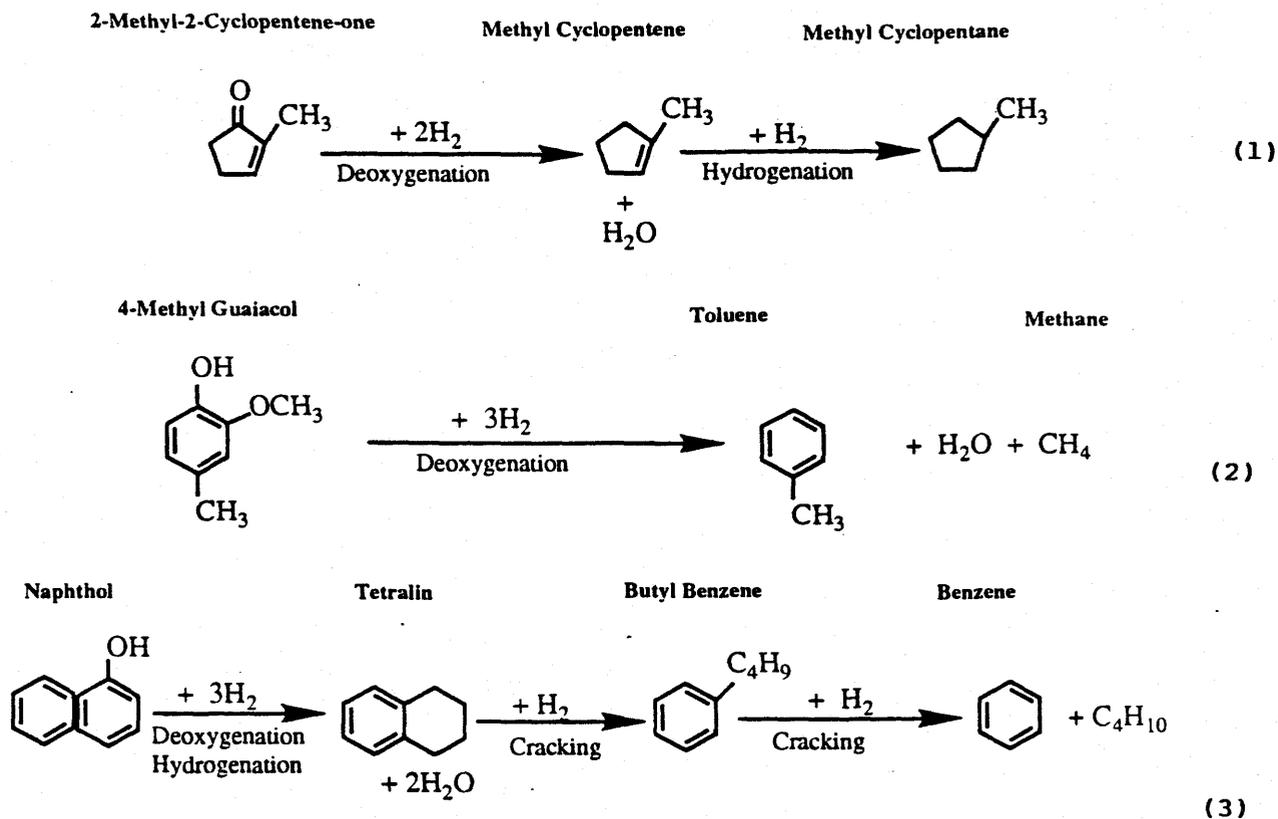


Figure 2.12 Model structures required for production of liquid hydrocarbons over hydrotreating catalysts [Baker and Elliot, 1987].

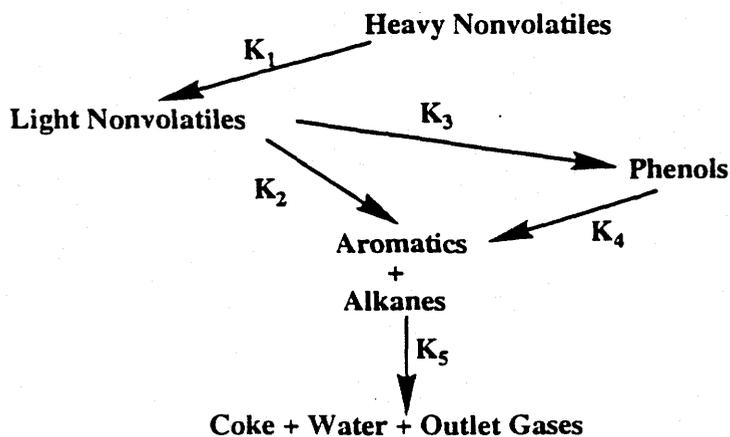


Figure 2.13 Lumped kinetic scheme for hydroprocessing of pyrolysis oil in trickle bed reactor [Soltes and Lin, 1987].

Figure 2.13. However, no comments were made on this scheme.

Sheu et al. [1988] also proposed a reaction scheme for the conversion of pyrolysis oil over commercial Co-Mo, Ni-Mo and Pt/Al₂O₃ hydrogenating catalysts. The products were divided into phenols, hydrocarbons, heavy and light non-volatiles, coke, water and light gases. It was suggested that the non-volatiles were cracked to both phenols and hydrocarbon compounds. The phenols were then converted to hydrocarbons which led to the formation of coke and light gases.

2.6.2 Chemical Kinetics

Usually, obtaining reaction pathways/mechanisms is the first step of the modeling process. The second step, which is centred on chemical kinetics, emphasises the dynamics or rates of the reactions. Chemical kinetics and reaction mechanisms are directly related [Moore and Pearson, 1981].

Rate is usually defined as the change in concentration of any reactant or product with time. For catalytic systems it is usually defined as Km³ol/Kg-cat.h. In fixed bed operations, rate data are obtained by carrying out experiments using either differential or integral reactor [Levenspiel, 1971; Espenson, 1981]. When conversions are high and the rates vary over the catalyst, the integral reactors are used. Data acquisition is usually determined for specific reactant concentration and used to determine rate as a function of concentration. For this system the equation for obtaining the

rate takes the differential form:

$$(-r) = F_1 \frac{dX}{dW} \quad (2.11)$$

[Levenspiel, 1977; Fogler, 1986]

From this the rate-concentration data is obtained.

Rate Laws

This is an important area in chemical kinetics where algebraic expressions are determined to describe rate as a function of the active components of the system such as concentration and temperature. Rate expressions are derived to describe the functional change in the rate when the concentration of all active species in the reaction mixture are varied [Froment and Bischoff, 1979; Moore and Pearson, 1981; Fogler, 1986].

Two widely used rate expressions are available in the literature. These are:

1. rate expressions that are of the form of a product of powers of concentrations (i.e. power law model):

$$-\frac{dC_A}{dt} = KC_A^a C_B^b \dots \quad (2.12)$$

[Carberry, 1976, Fogler, 1986]

2. rate expressions that are derived based on adsorption-

reaction-desorption postulates of rate mechanisms. A widely used form is the Langmuir-Hinshelwood-Hougen-Watson model [Carberry, 1976; Kam and Hughes, 1979] which is of the form

$$-\frac{dC_A}{dt} = \frac{KC_A^a C_B^b \dots}{[1 + k_A C_A^a + k_B C_B^b \dots]^n} \quad (2.13)$$

For elementary reactions the popular Arrhenius equation

$$K = K_0 e^{-\frac{E}{RT}} \quad (2.14)$$

is often used to study the influence of temperature on the rate, rate constant or adsorption coefficients [Westerterp et al., 1984; Fogler, 1986].

2.6.3 Kinetic Parameter Estimation

In kinetic investigations, it is not known a priori what the rate controlling step is and what the values of the rate constants, reaction orders, activation energies, and adsorption coefficients are. The determination of values for these parameters which are consistent with experimental data for each reaction pathway is termed the kinetic parameter estimation [Froment and Bischoff, 1979]. Estimation of the parameter values carries with it a number of advantages such as selection of reaction conditions such as temperature and concentrations for optimum product yields or selectivities. For instance, a negative order kinetics implies small

concentrations of reactants would favour product formation. Also, observations such as changing activation energies could provide information on the complexity of the reactions.

2.6.4 Reactor Design and Prediction of Yields from Models

The main reactor configuration used in the upgrading of wood-oils has been the fixed bed reactor. There are a vast number of mathematical models used for designing fixed bed reactors [Carberry, 1976, Froment and Bischoff, 1979]. These have been categorised into two main groups; pseudo-homogeneous and heterogeneous. Pseudo-homogeneous models do not account explicitly for the presence of catalysts, whereas heterogeneous models lead to separate equations for fluid and catalyst. The basic model used in most studies is the pseudo-homogeneous one-dimensional model which considers transport by plug flow in the axial direction. This model assumes that concentration and temperature gradients only occur in the axial direction, and flow is the only transport operating in this direction. This model is widely used because it is usually sufficient to represent most processes and also convenient to use. The conservation equation for this type of flow are

$$-U_s \frac{dC_A}{dz} = \rho_B r_A \quad (2.15)$$

(2.16)

$$U_s \rho_B C_p \frac{dT}{dz} = (-\Delta H) \rho_B r_A - 4 \frac{U}{d_t} (T - T_r)$$

with initial conditions: at $z = 0$; $C_A = C_{A0}$; $T = T_0$

This system of equations permits easy solution on a computer and simulation of the reactor.

However, if the flow in the reactor deviates from the ideal pattern because of radial variations in flow velocity and mixing effects due to the presence of catalyst, this model takes the form

$$\epsilon D_{ea} \frac{d^2 C_A}{dz^2} - U_s \frac{dC_A}{dz} = \rho_B r_A \quad (2.17)$$

$$\lambda_{ea} \frac{d^2 T}{dz^2} - U_s \rho_B C_p \frac{dT}{dz} = (-\Delta H) \rho_B r_A - 4 \frac{U}{d_t} (T - T_r) \quad (2.18)$$

The generally used boundary conditions are:

$$U_s (C_{A0} - C_A) = -\epsilon D_{ea} \frac{dC_A}{dz} \quad (2.19)$$

for $z = 0$

$$\rho_s U_s C_p (T_0 - T) = -\lambda_{ea} \frac{dT}{dz} \quad (2.20)$$

$$\frac{dC_A}{dz} = \frac{dT}{dz} = 0 \quad (2.21)$$

for $z = L$.

Two-dimensional pseudo-homogeneous models which account for resistance to heat and mass transfer in the radial direction and which predicts the detailed temperature and conversion patterns in the reactor are also available [Froment and Bischoff, 1979].

Heterogenous reactor models are also available [Froment and Bischoff, 1979]. These are of one and two-dimensional types. These models are useful for very rapid reactions with important heat effects and where it is necessary to distinguish between conditions in the fluid and on the catalyst.

2.6.5 Hydrocarbon Selectivity Relations

The composition of a reaction mixture for complex feeds such as gas oils and wood-oils, and whose consumption involves multiple reactions are described by either the conversion, yield or selectivity parameter. Calculation of the conversion for wood-oils is complicated and unreliable due to the vast number of components and the interconversion of compounds during reaction. On the other hand, the yield and selectivity of the desired product is simpler and a straight forward calculation is possible. The selectivity parameter has a

number of advantages because unlike the conversion, it can be manipulated in various ways to optimize the desired product and minimize the undesired one [Smith, 1970; Wojciechowski and Corma, 1986]. Knowledge of the selectivity parameter can also aid in selection of reactors and development of efficient processing schemes.

The selectivity parameter, S_p is defined as

$$S_p = \frac{I_D}{I_{UD}} \quad (2.22)$$

[Fogler, 1986; Wojciechowski and Corma, 1986].

2.6.6 Catalyst Deactivation

Rate model for deactivation

One of the most insidious problems in wood-oil processing is the loss of catalyst activity which occurs due to the accumulation of coke resulting in rate changes as the reaction proceeds. Similar to gas oil processing, deactivation by coking can be assumed to occur by the blocking of active sites [Decroocq, 1984]. In this case the rate of the main reaction



is assumed to be proportional to the unblocked sites so that the rate takes the form

$$r = KC_A^n(1-\phi) \quad (2.24)$$

Three major forms of deactivation are possible in wood-oil processing: series, parallel or independent deactivation.

In series deactivation, the sites are blocked by a product, C, formed by reaction of B, that is



Carbon deposition in hydrocarbon cracking where some of the primary products react further to coke is an example of series deactivation.

Parallel deactivation occurs when reactant A can react either by depositing carbon, C, on the active sites or by forming the desired product, B, by equation 2.25.

Independent deactivation occurs when the reactants or "impurities" poison the active sites by depositing on them. In wood-oil processing this could be done by the presence of Conradson carbon or highly non-volatile matter.

In all these cases, reaction rates for deactivation will be proportional to the concentration of B and the fraction of active sites, and would take the form

$$r_c = K_B C_B (1-\phi) \quad (2.26)$$

Empirical Models for Coke Formation

A number of empirical models have been derived to establish a relation between coke concentration and time. Two common models are:

1. those that express the amount of coke, C_c , on the surface as a function of time, t :

$$C_c = At^n \quad (2.27)$$

where C_c is the concentration of coke and A and n are constants.

2. those that establish a relationship between the catalyst activity and amount of coke. The commonly used form is

$$a = \frac{1}{C_c^p + 1} \quad (2.28)$$

where a is the activity and p is a constant [Fogler, 1986].

3.1

EXPERIMENTAL

3.1 Scope

The design, construction and operation of the fixed bed reactor and apparatus used to obtain data in this work are described in this chapter. Details of catalyst preparation and characterization as well as the procedures and experimental details of each phase of the research are also described in this chapter.

3.2 Fixed Bed Micro-reactor

The fixed bed micro-reactor was chosen for this work because of its simplicity of construction and operation as well as ease of analysis of reactions involving feeds of complex nature. Using fixed bed upgrading reduces the number of operating conditions or variables that need to be monitored on the process compared to fluidized or trickle bed reactors.

The reactor was constructed to approach isothermal behaviour by keeping the amount of catalyst as low as possible. The rise in temperature due to the reaction can then be assumed to be negligible. Also, by keeping the ratio of the diameter of reactor to diameter of catalyst greater than 30, axial dispersion can be assumed negligible and plug flow behaviour approached.

Details of the fixed bed reactor are shown in Figure 3.1. The fixed bed reactor (400 mm long) was constructed from 12.7 mm ID, SS 316 tubing. The catalyst was supported on quartz

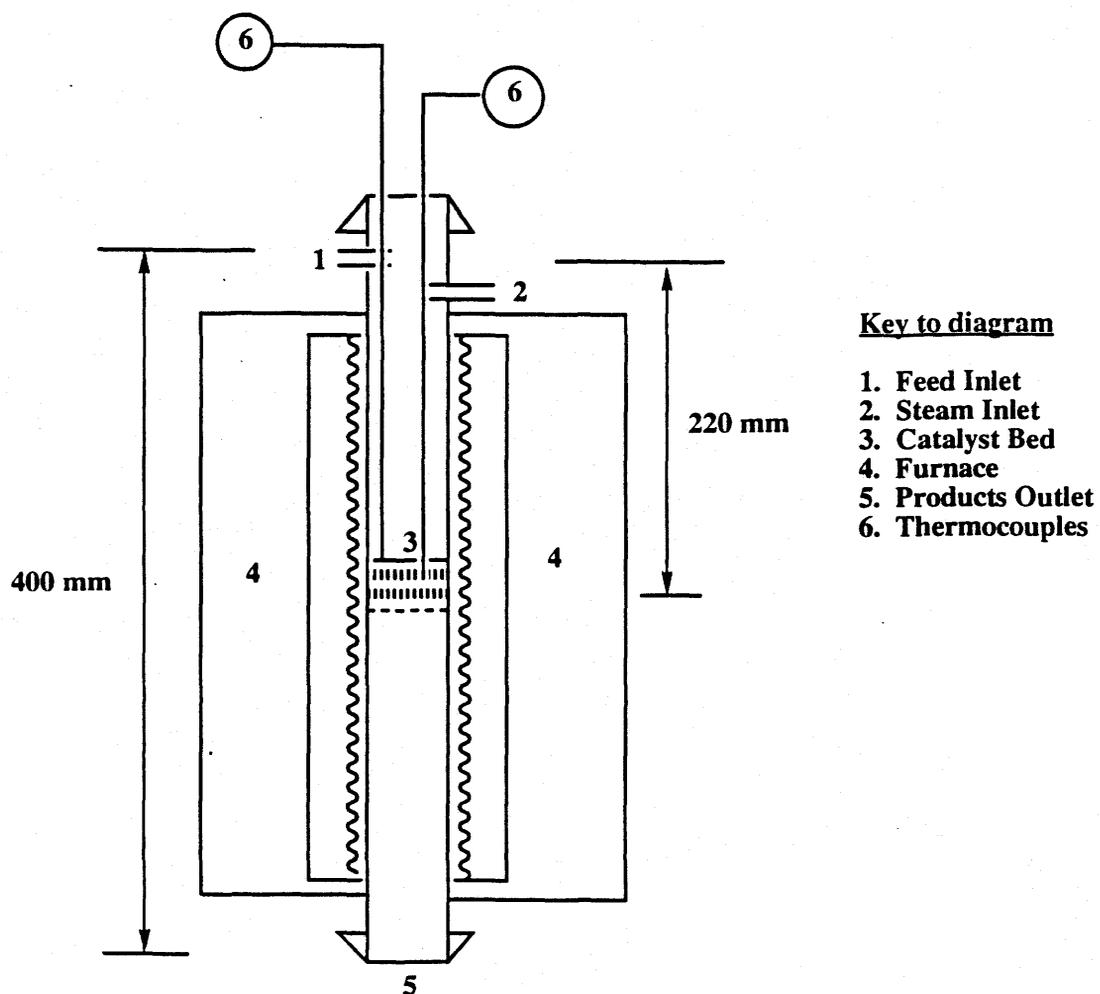


Figure 3.1 Details of fixed bed micro-reactor

wool which was placed on a mesh screen located 220 mm below the reactor inlet. The temperature of the bed was controlled by placing two K-type thermocouples, one at the top (connected to the indicator) and the other at the centre (connected to the controller) of the catalyst bed. The catalyst bed was about 30 mm long and the temperature difference between the top and centre did not vary by more than 1.5 °C.

3.3 Apparatus

The flow diagram of the apparatus used for upgrading the wood-oil and other reactants is shown in Figure 3.2.

The set up consists of two syringe pumps (Eldex A-60-S) connected to feed reservoirs. The pumps were capable of pumping fluids at flowrates between 0.3 and 30 mL/h. These reservoir may contain wood-oil, water or other reactants such as model compounds. The pumps were calibrated for their flow rate for each feed or compound. The pumps were connected by 1/8" stainless steel tubing to the inlet of the reactor. The connection was made in such a way that dripping along the walls of the reactor was kept to a minimum. The reactor was placed co-axially in a furnace. The reactor and furnace were used for both upgrading of the wood-oil and regeneration of the catalyst.

Two condensers connected in series were used to cool the products leaving the reactor. The first one used water flowing counter-current to the flow of products. The other was an ice-

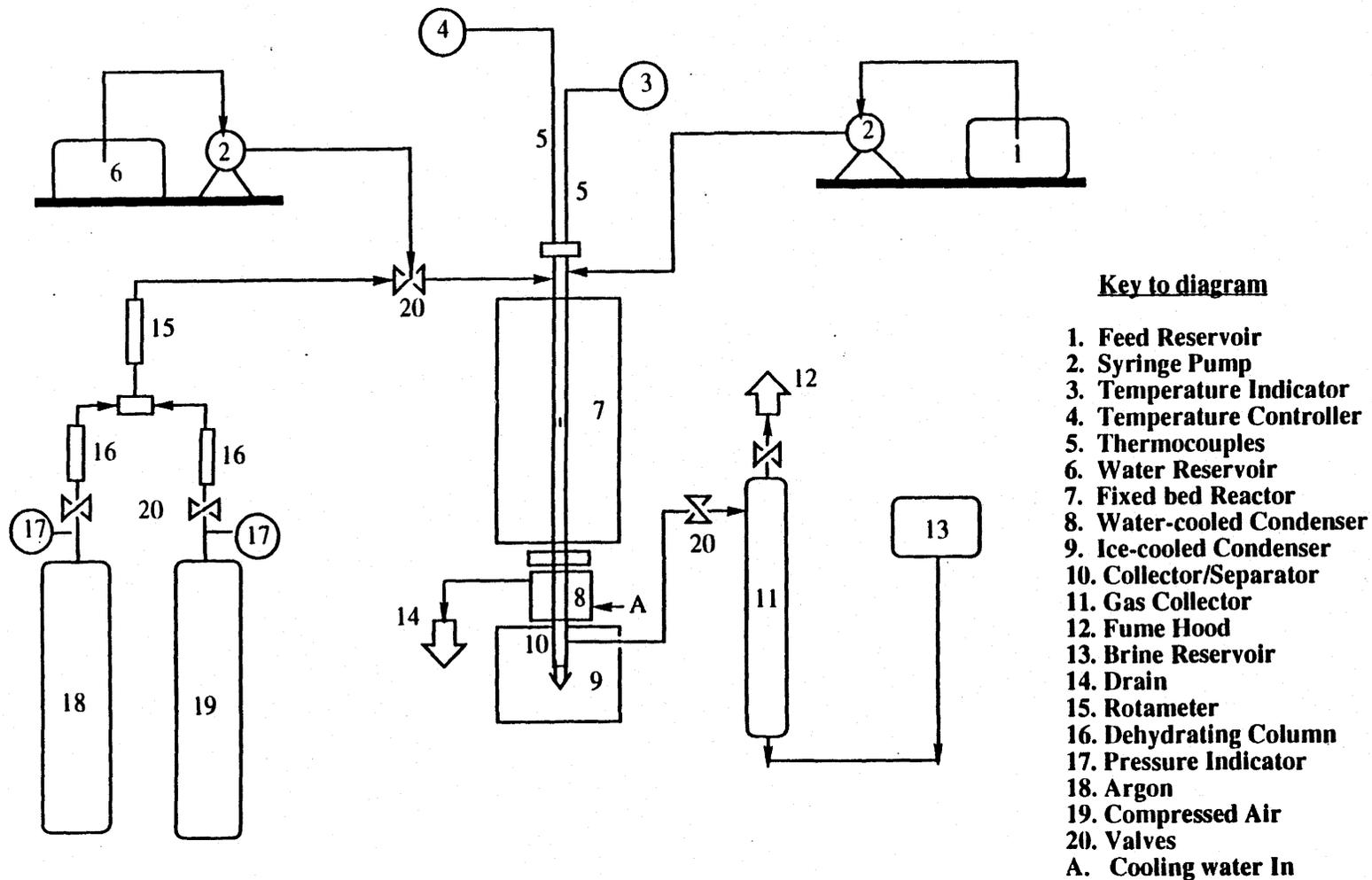


Figure 3.2 Schematic diagram of experimental apparatus for upgrading wood-oil.

cooled bath. A liquid product collector which also served as a separator was constructed to fit directly at the exit of the reactor and extended through the two condensers. It was calibrated so that readings could provide direct measurement of the volume of products collected.

The gas products leaving the reactor were collected over a solution of brine, saturated NaCl solution. The volume of brine displaced represented the volume of gas produced.

3.4 Procedure for Upgrading

The reactor was operated in a continuous downflow mode. The entire upgrading, product collection and analysis scheme is shown in Figure 3.3. A typical run was carried out as follows: The reactor was first loaded with catalyst and brought to the reaction temperature in a stream of argon flowing at 2 l/h. When the desired temperature was attained, the argon flow was stopped and the syringe pump was started. The length of each run was determined by process time studies.

The reaction products leaving the reactor were separated into liquid and gas products. The liquid product consisted of an aqueous and an organic phase. This was trap cooled by the condenser and then separated. The organic fraction was distilled under vacuum at 200 °C and 172 Pa using a Buchi GKR-56 distillation unit. It was determined in experiments on the vacuum distillation characteristics of the wood-oil that these conditions produced the maximum organic distillate. The vacuum

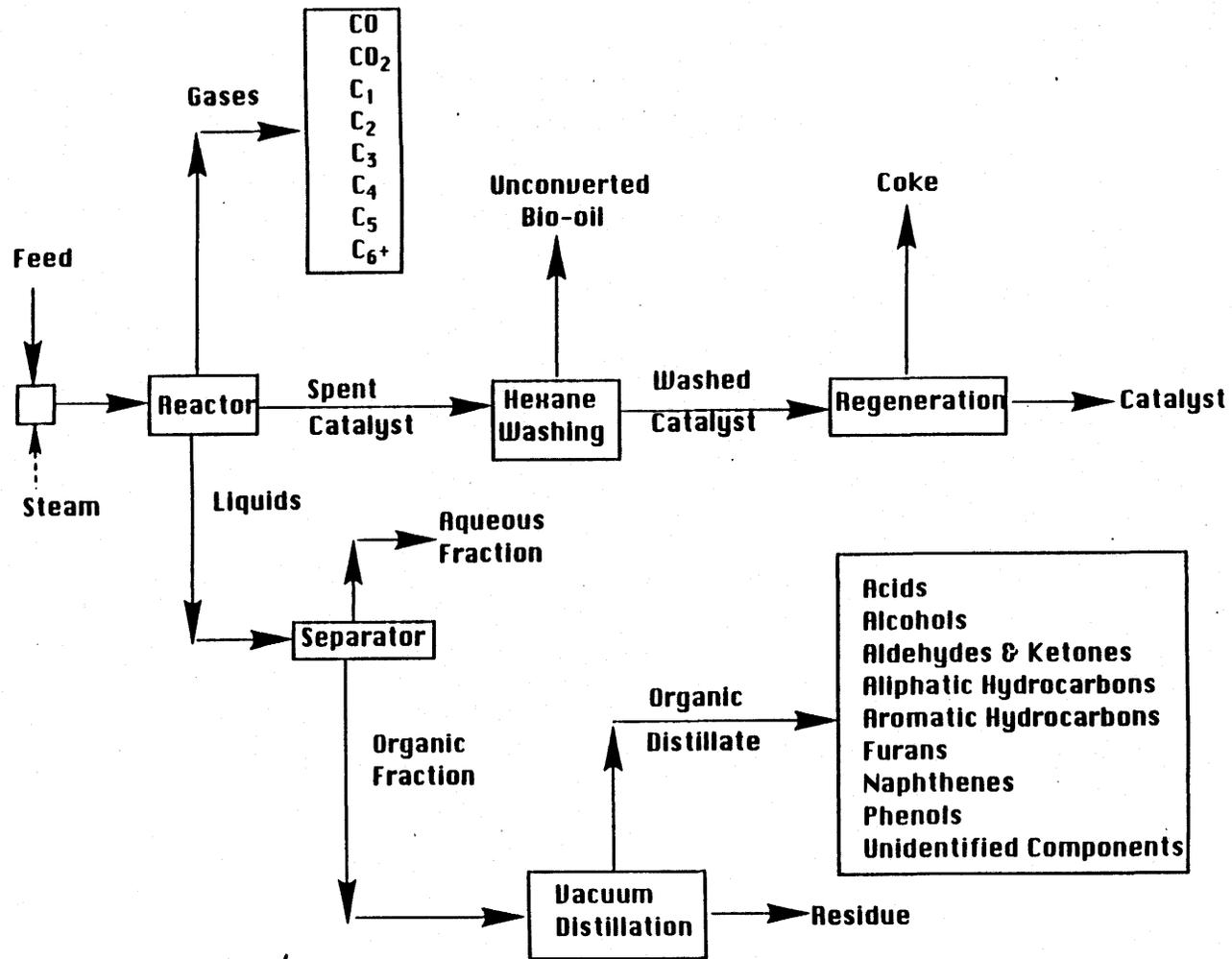


Figure 3.3 Upgrading, product collection and analysis scheme.

distillation produced two fractions; a volatile and non-volatile fraction which were identified as the "organic distillate" and "residue", respectively.

The gas produced was collected over the brine solution and the volume was determined. After each run, the spent catalyst was removed from the reactor and the material deposited on it was assumed to be coke and unconverted feed. Following this, the spent catalyst was washed with hexane. Similarly, the inside surface of the reactor was washed with hexane. The hexane-soluble portion was designated as "unconverted oil" (or tar) where wood-oil was used and "unconverted reactant" where reactants such as model compounds were used. The washed catalyst was then dried at 100 °C for 1 h followed by heating in an air flow for about 1 h at 600 °C to regenerate it. The difference in weight before and after regeneration of the washed catalyst was termed "coke".

The experimental set-up and procedure described above were used in experiments in phases 2 to 6. The experimental set-up and procedure for phase 1 are described in section 3.6.1.

3.5 Analysis

A number of different analytical procedures and methods were used to determine the composition of the products and in some situations the reactants. These included CHN analysis (elemental), Karl Fischer titration, GC and GC-MS analyses.

Most of the gas and liquid product analyses were based on GC measurements using Carle CGC, model 500.

The Carle CGC has been designed to analyze C_1 - C_5 hydrocarbons and permanent gas. The C_1 - C_5 hydrocarbons and permanent gases were analyzed by the thermal conductivity detector (TCD). Simultaneously, the hydrocarbons were being analyzed by the Flame Ionization Detector (FID) utilizing its greater sensitivity to be able to trace hydrocarbons not detected by the TCD. Sequentially, a second sample was injected onto a 50 m capillary column to analyze the C_6 and higher hydrocarbons. A loop isolation valve was provided to hold the sample for capillary analysis. The analysis on this GC is shown schematically in Figure 3.4.

Organic Distillate Analysis by GC

The organic distillate was analyzed using the 50 m long fused silica capillary column and the FID. The temperature in the GC oven was programmed from 50 to 200 °C and an analysis took approximately 45 min.

Identification of the various peaks were carried out by two main methods. One involved using a GC-MS analysis procedure. Samples of the organic liquid product were analyzed on a Flannigan/MAT 4500 GC-MS at the National Research Council under the same chromatographic conditions as used on the Carle GC. The data system on this unit scanned the mass spectra from M_z 43 - 510 at 1 scan/sec analysis and provided a list of

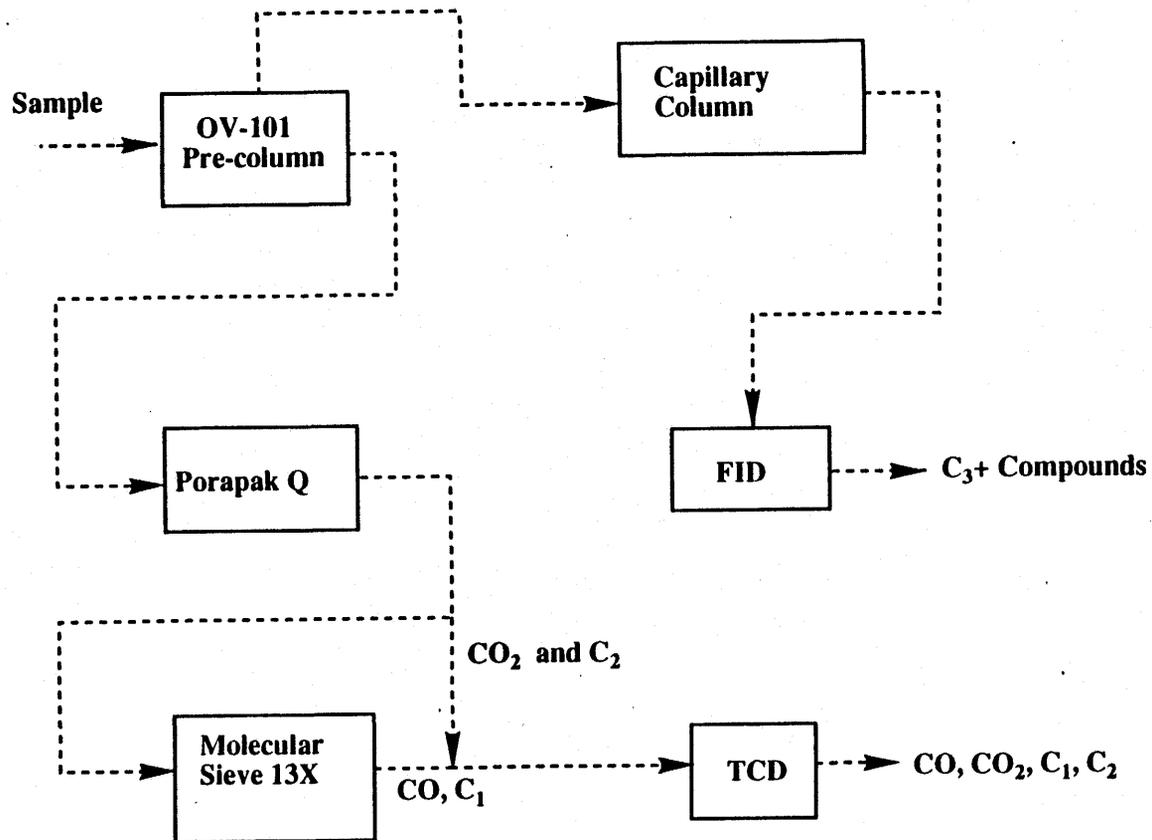


Figure 3.4 Product analysis by Carle gas chromatograph

probable compounds for each peak in order of the probability of their occurrence. The second method involved the calibration by determining the retention times of various concentrations of pure compounds and mixtures of compounds of known composition using the Carle GC operating under the same chromatographic conditions. Some of these compounds are shown in Table 3.1. Some of the calibration mixtures were obtained from PolyScience Corporation and others were prepared in the laboratory. These mixtures included mixtures of alcohols, hydrocarbons, ketones, methyl and ethyl esters of organic acids. Also, mixture comprised of different chemical groups were prepared and used for calibration. Typical hydrocarbon calibration mixtures are presented in Table 3.2.

Also, information of retention of various compounds in the literature were used as an aid to identify the peaks.

For each analysis, the individual compounds identified were placed under similar chemical groups. These groups included acids, alcohols, aldehydes and ketones, aliphatic hydrocarbons, aromatic hydrocarbons, furans and phenols as shown in Figure 3.3. Those peaks which could not be identified under the available data base were termed the "Unidentified components". A Typical chromatogram and peak identification are presented in Appendix B.

Table 3.1
Some of the compounds used for calibration and preparation of calibration mixtures.

| | | |
|----------------------------|--------------------------------|-----------------------------|
| 2-Methylpentane | Toluene | |
| 3-Methylpentane | o-Xylene | Cyclopentanone |
| 2,2-Dimethylbutane | m-Xylene | 2-Methyl cyclopentanone |
| 2,3-Dimethylbutane | p-Xylene | 2-methyl cyclohexanol |
| 3-Methylhexane | Ethylbenzene | |
| 2,3-Dimethyl- pentane | 1,2,4- Trimethylbenzene | Methyl ester acetic acid |
| 2,4- Dimethylpentane | 1,2,4,5- Tetramethylbenzene | Propanoic acid |
| 3-Methylheptane | p-Cymene | |
| 2,5-Dimethylhexane | n-Propylbenzene | |
| 2,2,4- Trimethylpentane | n-Butylbenzene | |
| n-Hexane | n-Hexylbenzene | |
| n-Heptane | n-Octylbenzene | |
| n-Octane | n-Decylbenzene | |
| n-Nonane | Cumene | |
| n-Decane | Mesitylene | |
| n-Undecane | | |
| n-Dodecane | Phenol | |
| n-Tridecane | Eugenol | |
| n-Tetradecane | Methoxybenzene | |
| n-Pentadecane | Ethoxybenzene | |
| n-Hexadecane | Cyclohexane | |
| n-Heptadecane | 3-Methylpentane | |
| n-Octadecane | 1-Hexanol | |
| n-Nonadecane | 1-Pentanol | |
| Benzene | Isobutyl alcohol | |

Table 3.2

Typical hydrocarbon calibration mixtures used for analysis (PolyScience Corporation).

| Compound | Wt% | Compound | Wt% |
|------------------------|-------|------------------|-------|
| <u>Mixture A</u> | | <u>Mixture D</u> | |
| n-Dodecane | 24.62 | 1-Decene | 6.67 |
| n-Tridecane | 24.86 | 1-Undecene | 13.33 |
| n-Tetradecane | 25.09 | 1-Dodecene | 20.00 |
| n-Hexadecane | 25.42 | 1-Tridecene | 26.67 |
| | | 1-Tetradecene | 33.33 |
| <u>Mixture B</u> | | <u>Mixture E</u> | |
| 2-Methylpentane | 13.86 | Ethylbenzene | 80.00 |
| n-Hexane | 24.50 | n-Octadecene | 2.00 |
| 2,2,4-Trimethylpentane | 32.71 | n-Nonadecene | 5.00 |
| Dimethylhexane | 13.36 | n-Heneicosane | 6.00 |
| 2,2,5-Trimethylhexane | 15.57 | n-Docosane | 7.00 |
| <u>Mixture C</u> | | <u>Mixture F</u> | |
| 1-Pentene | 14.65 | Benzene | 21.56 |
| 1-Hexene | 11.93 | Toluene | 25.23 |
| 1-Heptene | 37.53 | m-Xylene | 20.14 |
| 1-Octene | 15.38 | o-Xylene | 18.99 |
| 1-Nonene | 20.51 | p-Cymene | 14.08 |

Gas Analysis by GC

The gaseous products were also analyzed by GC using a combination of packed and capillary columns (Figure 3.4). The sample was injected onto a 2 m long pre-column, packed with OV-101 silicone oil. All components lighter than ethane passed rapidly through this column, then the C₃+ components were backflushed onto the fused silica capillary column. Ethane and the lighter components were then passed through a 2 m porapak Q and a 3 m molecular sieve 13X column to separate C₁, C₂, CO and CO₂ which were measured by TCD. The C₃+ components were measured by FID. After normalization of the components, an average molecular weight was calculated for the gaseous product. The weight of the gas fraction was determined from the average molecular weight and the total volume of the gas evolved during the run.

The identity of the peaks were determined using pure compounds and mixtures of compounds of known composition.

3.6 Experiments Under Each Phase

3.6.1 Phase 1: Preparation, Distillation Characteristics and Stability Studies of Wood-oil.

Wood-Oil Preparation

The raw material used in this study was aspen poplar (*Populus tremuloides*, obtained from poplar bluffs near Saskatoon) wood. The wood-oil was prepared following the procedure described by Eager et al. [1982]. The wood was in the form of air dried powder, less than 1 mm in diameter. The liquefaction was carried out in a pressure reactor consisting of an AMINCO high pressure autoclave, model 406-010A, a shaking assembly with $1.41 \times 10^{-3} \text{ m}^3$ reaction vessel. The temperature was measured with an iron-constantine thermocouple and controlled to $\pm 5 \text{ K}$ by a Brown Electric Pyrometer. Pressures were measured to an accuracy of $\pm 2\%$ by a Validyne pressure transducer and modulator, and displayed as a digital readout.

The following procedure was followed for each reaction. Wood powder (100 g-dry basis) and a solution containing 10 g sodium carbonate (catalyst) in 500 mL water were added to the reaction vessel. The wood meal and solution were thoroughly mixed. With the reactor in the shaking assembly, carbon monoxide (Liquid Carbonics, 99.5 % pure) was used, first to flush out the reactor and then to pressurize it to about 5

MPa. The shaking assembly and heater were then started; a time of approximately 2.5 h was required to bring the reactor to the 360 °C, the desired operating temperature. It was maintained at this temperature for 2 h, stopped and contents allowed to cool which normally took about 4 h. After the reactor has cooled to room temperature, the gases were vented.

The liquid product consisted of an aqueous phase and an oil phase. The aqueous phase was decanted. It was initially colourless but underwent a series of colour changes through yellow to a reddish brown and finally to a deep blue black colour in about 15 s. The yield of the oil phase, i.e., the wood-oil, was 30 g.

Karl Fischer titration (Appendix C) of the fresh wood-oil showed that it contained 1.5 wt% water. Elemental analysis showed that carbon, hydrogen and oxygen (determined by difference) contents of the wood-oil were 70.9, 8.8 and 20.3 wt.%, respectively. No nitrogen could be detected in the CHN analyses. Several batches of wood-oil were produced for characterization and stability studies. For stability measurements, four of these were stored in separate 30 mL bottles, filled to the top and stoppered. The bottles were covered with aluminium foil to prevent exposure to light. Two of these contained wood-oil+tetralin mixtures in a 2:1 weight ratio and the other two contained only wood-oil. Various characterization measurements (density, viscosity and vacuum distillation) were made in duplicate from these bottles and

the average values determined. For each analysis about 15 mL of the wood-oil was removed and once the measurements were completed 9 mL was returned. The bottle was kept stoppered all the time. Thus, the wood-oil was exposed to a very small amount of air during storage.

Distillation Characteristics Studies

The distillation characteristics of the fresh wood-oil were used for characterization studies as well as a reference for distillates from oils of different ages in the stability monitoring studies.

About 4 g of the fresh wood-oil were distilled over the temperature range 85-250 °C in a Buchi GRK-50 distillation unit for 30 min under a fixed vacuum of 172 Pa. The distillate was collected in a bulb immersed in liquid nitrogen and was analyzed by gas chromatography. The amount of non-volatile residue remaining after the distillation was determined.

Stability Studies

The stability of the wood-oil was studied by following the changes in density, viscosity, distillation characteristics and chemical composition of the wood-oil and wood-oil-tetralin feed mixture. In addition, elemental analyses of the distillate and residue fractions were carried out.

4 g of fresh wood-oil were distilled under a vacuum of 172

Pa at 175, 200 and 250°C. The density, viscosity, distillation characteristics and the distillate composition were measured on days 1, 16 and 31. To study the effect of tetralin addition on stability, tetralin and wood-oil were mixed in a 1:2 weight ratio. Samples of the mixture were distilled under vacuum at 175, 200 and 250 °C on days 1, 16 and 31. Similarly, the amounts of residue and distillate and the composition of distillate were determined. The viscosity and density measurements were also made at the above time intervals.

The density and viscosity measurements were carried out at 25 °C using a 10 mL pycnometer and Brookfield cone and plate digital viscometer (model RVTDCP), respectively. The elemental analyses of the distillate and residue fractions, obtained at 172 Pa and 200 °C were performed on a Perkin Elmer 2400 CHN Analyzer.

3.6.2 Phase 2: Catalytic Upgrading of Wood-oil, and Regeneration Studies Using HZSM-5 Catalyst.

Experiments in this section consisted of blank runs (thermal studies) on the oil, tetralin reactivity, process time, temperature and regeneration studies. These are discussed below:

Blank Runs (Thermal Conversion) of Wood-oil

These runs comprised the heat treatment of the feed using the reactor packed with inert berl saddles and conducted over the temperature range 290 to 410 °C. This was also carried out at 3.6 weight-hourly space velocity (WHSV) and run time of 30 min. The product collection and analysis scheme followed the same procedure as described previously.

Tetralin Reactivity Over HZSM-5

These experiments were carried out in order to investigate the reactivity of tetralin since it was used both as a diluent and hydrogen-donor solvent. For this purpose, tetralin was contacted with the HZSM-5 catalyst at 3.6 WHSV and temperature range 290 to 410 °C. The effect of tetralin conversions on the product from upgrading were later taken into account.

Process Time and Temperature Studies

The objective was to study the effect of length of experimental run and temperature on the yield of the desired organic distillate and the selectivity for hydrocarbons. The process time studies were used as a basis for the selection of 30 min as the best run time for upgrading. In these runs the feed was processed with the catalyst at run times of 15, 30, 45 and 60 min and reaction temperature 370 °C. For temperature studies, experimental runs were carried out over the range 290

to 410 °C. Each run was set at 30 min.

Effect of Using Regenerated Catalyst

Studies were also conducted on the upgrading of wood-oil using regenerated catalyst. This was carried out in order to evaluate the performance of the catalyst during the wood-oil upgrading in terms of its regeneration. During these studies, the spent catalyst was regenerated in an air flow at 600 °C for 1 h, and then used for upgrading of the wood-oil at 370 °C. This process was repeated until the catalyst was used four times. The overall product distribution, distillate composition and the elemental composition of the distillate were monitored. In addition, x-ray diffraction and BET surface area analyses were performed on the catalyst.

3.6.3 Phase 3: Effect of Co-feeding Steam

The same set of experiments conducted in phase 2 were carried out here. However, in these runs the wood-oil was processed in the presence of steam which was co-fed with the wood oil in a 1:1 weight ratio. Blank runs, tetralin reactivity, process time, temperature and regeneration studies were conducted in the presence of steam. The data collected were calculated on a steam and tetralin-free basis.

3.6.4 Phase 4: Conversion and Performance of Other Catalysts in Upgrading Wood-oil

In this phase of the research the conversion of wood oil to fuels and chemicals were carried out using silicalite, H-mordenite, H-Y and silica-alumina catalysts. The synthesis and characterization of these catalysts are described in section 3.7. First, tetralin reactivity over these catalysts was studied. This was later taken into account during the analysis of the products. Following this the effect of temperature (330-410 °C) was studied. The procedure and analyses followed the same format as described earlier. The pore size, acidity and shape selectivity characteristics were also set as experimental variables. Runs were set at 3.6 WHSV.

3.6.6 Phase 5: Model Compound Studies and Reactions of Synthetic and Wood-oil Volatile Fractions.

In this phase of the research, reactivity data were obtained for the conversion of model compounds: propanoic acid, 4-methylcyclohexanol, cyclopentanone, 2-methylcyclopentanone, methyl ester acetic acid, methoxybenzene, ethoxybenzene, phenol and 2-methoxy-4(propenyl) phenol (eugenol) over HZSM-5 catalyst. These were used as models to represent the chemical groups: acids, alcohols, aldehydes and ketones, esters, ethers and phenols.

A synthetic volatile fraction was also prepared from six model compounds representing the six chemical groups and upgraded with the HZSM-5. This mixture contained 2.2 wt% propanoic acid, 1.0 wt% methyl ester acetic acid, 6.9 wt% 4-methylcyclohexanol, 14.6 wt% 2-methylcyclopentanone, 13.6 wt% ethoxybenzene, and 61.7 wt% eugenol. These compositions were the proportion in which the chemical groups occurred in the volatile fraction when distillation was conducted on the wood oil at 200 °C and 172 Pa.

Also, the wood-oil volatile fraction was treated with HZSM-5 catalyst. The wood-oil volatiles were obtained by fractionation of the whole wood-oil at 200 °C and 172 Pa following the procedure described in phase 1.

The model compounds and volatile fractions were fed in the pure state and three other concentrations prepared by mixing with tetralin. In all cases, the conversion of tetralin to reaction products were accounted for. The detailed experimental conditions are presented in Table 3.2.

3.6.6 Phase 6: Experiments for Obtaining Rate-concentration Data.

The objective was to collect rate-concentration data for each path of the reaction pathways derived from the experiments described in phase 5 and shown in Figures 4.35 and 4.36. The procedure involved isolating the reaction networks

into three main parts and collecting data separately for each part. This is similar to the method of isolation or partial analysis of rate data [Levenspiel, 1971] or the method of competition experiments for intermediates [Swinbourne, 1971].

Data collection for paths 1 and 2 involved the vacuum distillation of the wood-oil to obtain volatile and non-volatile fractions. In this part it was assumed that in terms of concentration and composition, the volatile and non-volatile fractions obtained during the vacuum distillation were similar to those obtained when the wood-oil encountered the reaction temperatures just before contact with the catalyst. The complete experimental procedure for obtaining these fractions have been described in phase 1.

Another set of experiments was designed to obtain rate-concentration data for the paths 3 and 4 for Figure 4.35 and 3, 4 and 5 for Figure 4.36. This involved the upgrading of the non-volatile fraction obtained from the vacuum distillation of the wood-oil. This was carried out at various concentrations and temperature range of 330 to 410 °C (Table 3.3). The concentrations of volatiles (path 3), residue (path 4) and coke (path 5) were measured and rates calculated by equation 2.12 to obtain a series of rate-concentration data.

Table 3.3

Reaction conditions for processing model compounds and mixtures using HZSM-5 catalyst.

| Temperature range: 330-410 °C | | | | |
|--------------------------------------|---------------------------|------|------|------|
| Pressure: Atmospheric | | | | |
| WHSV: 3.6 h⁻¹ | | | | |
| Mass of Catalyst: 0.002 Kg | | | | |
| Feed | Concentration, wt% | | | |
| Propanoic acid | 100.0 | 18.4 | | |
| 4-methylcyclohexanol | 100.0 | 17.0 | | |
| Cyclopentanone | 100.0 | | | |
| 4-Methyl cyclopentanone | 100.0 | 36.6 | 13.2 | 6.2 |
| Methyl ester acetic acid | 100.0 | | | |
| Methoxybenzene | 100.0 | | | |
| Ethoxybenzene | 100.0 | 43.0 | 12.6 | 4.8 |
| Phenol | 14.7 | | | |
| 2-Methoxy-4-(2-propenyl)phenol | 100.0 | 43.0 | 16.7 | 6.2 |
| Synthetic Volatiles | 100.0 | 41.0 | 23.0 | 12.0 |
| Wood-oil Volatiles | 100.0 | 44.0 | 25.0 | 10.2 |
| Non-volatiles | 65.7 | 45.0 | 22.1 | 9.5 |

Also, another group of experiments were designed to obtain data for paths 5-8 (Figure 4.35) and 6-10 (Figure 4.36). This involved the upgrading of the volatile fraction obtained from the vacuum distillation of the wood-oil at different concentration and temperature range 330-410 °C and 3.6 WHSV. The concentration of the product gases, aqueous fraction, coke, residue and organic distillate was measured and the rates calculated according to equation 2.11.

By this method a series of rate-concentration data were obtained for each path of the reaction networks.

3.7 Catalysts

In this section, the bases for selection of catalysts used in this research are provided. Following this the structure, the method of preparation and the results obtained from the characterization of the catalysts are also presented.

Selection of Catalysts

The advantages of using zeolites compared to hydrotreating catalysts have already been mentioned in Chapter 2. For HZSM-5, it has already been mentioned that its proven ability to convert various oxygenated compounds to gasoline range hydrocarbons in addition to its regeneration capability and thermal stability served as the basis for its use as the primary catalyst in this research. Silicalite, H-Y, H-mordenite and Silica-alumina were also used as catalyst in this research. The principal objective of using these zeolite and non-zeolite catalysts was to determine the extent (performance) to which they could upgrade wood oil to hydrocarbon-rich liquid products since no information on the performance of these catalyst is available. In addition to conversion to hydrocarbon-rich products, the catalysts were chosen so that an investigation into the role of catalyst acidity, crystallinity (shape selectivity) or non-crystallinity, pore size and structure on the upgrading process could be made possible.

Silica-alumina catalyst was selected in order to

investigate the role of catalyst crystallinity (shape selectivity) and non-crystallinity on upgrading. Silica-alumina is amorphous, but the basic composition is comprised of similar alumina and silica compounds as the zeolites.

H-Y and H-mordenite were selected in addition to HZSM-5 so as to enable studies on the effect of pore size and structure on upgrading and distribution of products to be conducted.

Silicalite was selected in order for the role of catalyst acidity on upgrading to be evaluated. This is possible because silicalite possesses similar three dimensional framework and pore size as HZSM-5 with the only difference being the complete absence of acid sites.

The HZSM-5 used was synthesized following the procedure described by Chen et al. [1973]. The detailed preparation procedure is outlined in Appendix C. The structure of HZSM-5 catalyst has also been described in Chapter 2. Silicalite and H-mordenite catalysts were obtained from the Molecular Sieves Department of Union Carbide. H-Y and silica-alumina were obtained from Saskatchewan Research Council.

In the following sections the structure of silicalite, mordenite, H-Y and silica-alumina are described. Following these, the characterization by BET surface area, pore volume, pore size analysis and X-ray diffraction measurements of these catalysts are provided.

Structure of Silicalite

Silicalite is a silica composition of uniform pore diameter, which exhibits molecular sieve and hydrophobicity or organophilic, but not ion-exchange properties. It is free of all alumina and is a silica polymorph of ZSM-5 with a similar framework as ZSM-5. At ambient conditions it adsorbs molecules as large as benzene (kinetic diameter 5.85 nm) but rejects molecules larger than 6 nm (such as neopentane with kinetic diameter 6.2 nm) [Flanigen et al., 1978; Michiels and De Herdt, 1987].

Structure of Zeolite Y

Y type zeolite is a synthetic form of faujasite, a natural crystalline aluminosilicate zeolite with a chemical composition



The Y type zeolite is produced when the sodalite units (secondary building unit) of Figure 2.1 are joined through hexagonal faces (hexagonal prisms) forming a hexagonal ring containing 12 Si/Al and 12 oxygen atoms. This gives a basic access diameter greater than or equal to 0.74 nm as shown in Figure 2.4. These apertures are large enough to allow access to rather bulky molecules such as $(\text{C}_4\text{H}_9)_3\text{N}$, isoparaffins, cyclohexene and aromatics [Campbell, 1983; Michiels and De Herdt, 1987].

Structure of Mordenite

Naturally occurring mordenite has the general formula



(3.2)

The secondary building unit of mordenite is the 5-1 branched rings shown in Figure 3.5. These are interspersed with 4 member rings to form twisted 12 rings and joined together to form a two dimensional building sheet through the sharing of oxygen atoms. The framework is generated by the attaching of these sheets. The final structure involves wide 12 ring channels nearly cylindrical and 8 ring channels, and form effective aperture sizes of 6.7 x 7.0 on one face and 2.9 x 5.7 on the other. The main channel is similar to the dimensions of benzene and pyridine [Breck, 1984; Michiels and De Herdt, 1987].

Structure of Silica-alumina

The structure of silica-alumina is a silica tetrahedral lattice in which some of the silicon atoms have been replaced by aluminium atoms. The aluminium atoms in alumina are bonded to only three oxygen atoms, whereas the silicon atoms in silica are bonded to four oxygen atoms. This imbalance is resolved by silica forcibly accommodating each aluminium atom in its four-fold coordination using hydrogen atom derived from residual water content. Two main microscopic structures of silica-alumina are possible. These are the Lewis acid and

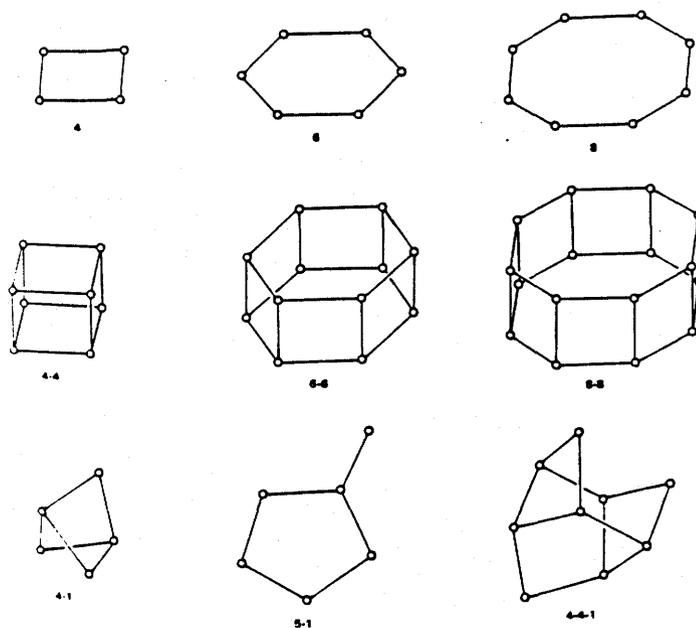


Figure 3.5. Secondary building units found in zeolite structures [Szostak, 1989].

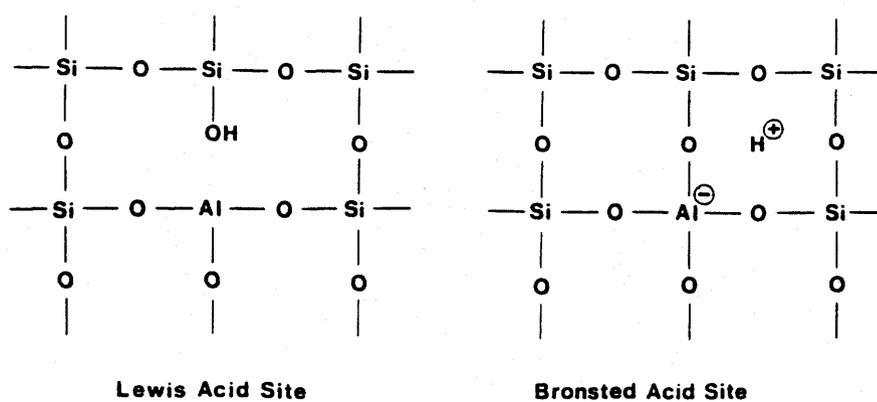


Figure 3.6. Representations of the Lewis and Bronsted acid sites in silica-alumina [Campbell, 1983].

the Bronsted acid structures and are shown in Figure 3.6 [Campbell, 1983].

Acidity of Silica-alumina

It has already been mentioned that two main microscopic structures are possible with silica-alumina. These are the Lewis and the Bronsted acid site structures.

In the Lewis acid structure which is shown in Figure 3.6a, an Al atom effectively takes up the tetrahedral configuration of bonds required by the silica lattice. But because Al has one electron less than Si, a fourth bond from Al cannot be formed and the resultant configurational vacancy represents a site where an electron pair can be accepted [Campbell, 1983].

In the Bronsted acid structure which is shown in Figure 3.6b, an electron is donated to the Al atom, allowing it to form the fourth bond, and the resultant negative charge is balanced by the presence of a proton (H^+) in its vicinity [Campbell, 1983].

Synthesis of Mordenite

A wide range of silica and alumina sources have been utilized for the synthesis of this zeolite, including natural and synthetic materials and resulted in zeolites with silica/alumina ratios between 9 and 11. Also, high ratios of silica/alumina have been prepared [Scott, 1980].

A typical preparation involving high silica/alumina ratios include using sources of silica, alumina, alkali metal and one or more neopentylamine. The reaction conditions are 80 to 210 °C and 70 to 400 psi/g [Michiels and De Herdt, 1987].

Synthesis of Zeolite Y

A typical Y zeolite [Michiels and De Herdt, 1987] with silica/alumina ratios between 2.5 and 6 is prepared by

1. forming a zeolite precursor reaction mixture containing silica, alumina, sodium hydroxide and water and crystallization initiating amorphous silica-alumina nucleation centres having a particle size below 0.1 micron.
2. heating the reaction mixture to a temperature of from 90 to 110 °C for a period sufficient to produce 15 to 100% crystallization.
3. diluting the reaction mixture with sufficient water to yield a sodium silicate solution concentration from 3 to 7 wt% SiO₂.
4. gelling the reaction mixture with an acid gelling mixture to produce an amorphous hydrogel composite.
5. washing and drying the said composite to produce a particulate catalyst.

Synthesis of Silicalite

This is prepared by crystallizing hydrothermally in a closed system a solution containing alkylammonium cations

(e.g. TPA), hydroxyl ions and a reactive form of silica at 100-200 °C followed by thermal decomposition (usually calcining in air at 500-600 °C) to remove the organic template and yield the microporous silica crystals [Flanigen et al., 1978].

Synthesis of Silica-alumina

This catalyst is prepared by dissolving silica and aluminium hydroxide in controlled proportions in sodium hydroxide solution followed by a gradual acidification with hydrochloric acid to form a gel at a pH of about 9. The gel is then filtered off, washed and dried at temperatures less than 127 °C followed by calcining at temperatures of the order of 727 °C [Campbell, 1983].

X-ray Diffraction Analyses

The results from X-ray diffraction analyses of the catalysts showing the most prominent peaks are presented in Tables 3.5 to 3.8. A typical diffraction pattern for HZSM-5 is shown in Figure 3.7. The X-ray diffraction analysis was obtained at the Saskatchewan Research Council with Philips diffractometer (Model No. PW1310) using CuK_α radiation with a glancing angle of 5-85 ° and scanning speed of 2°/min. The spacings and intensities of the peaks closely matched with the XRD patterns given in the literature [Breck, 1984; Michiels and De Herdt, 1987; Szostak, 1989] and presented in Appendix

A.

Surface Area and Pore Volume

BET surface area measurements, pore size and pore volume distributions were conducted with ASAP (Accelerated Surface Area and Porosimetry) 2000 Analyzer (Micromeritics) equipped with multi-tasking software control and a single and dual analyzers controls.

The pore sizes and maximum pore volume were calculated using the Horvath-Kawazoe equations and the micropore surface area by Dubinin-Astakhov equation [Micromeritics, 1992].

A summary of the important physical and chemical data for each catalyst are given in Tables 3.4 to 3.8.

Table 3.4

Important physical and chemical data for silica-alumina.

| | |
|--------------------------------|---|
| BET surface area | = 320.7 |
| Silica/Alumina ratio | = 0.79 |
| Chemical Analysis: | |
| SiO ₂ | = 41.0 |
| Al ₂ O ₃ | = 52.0 |
| TiO ₂ | = 2.2 |
| Na ₂ O | = 0.5 |
| Fe ₂ O ₃ | = 0.5 |
| Zeolite | = 11.8 |
| Activity stabilization: | Steam for 1 h at 732 °C and atmospheric pressure. |

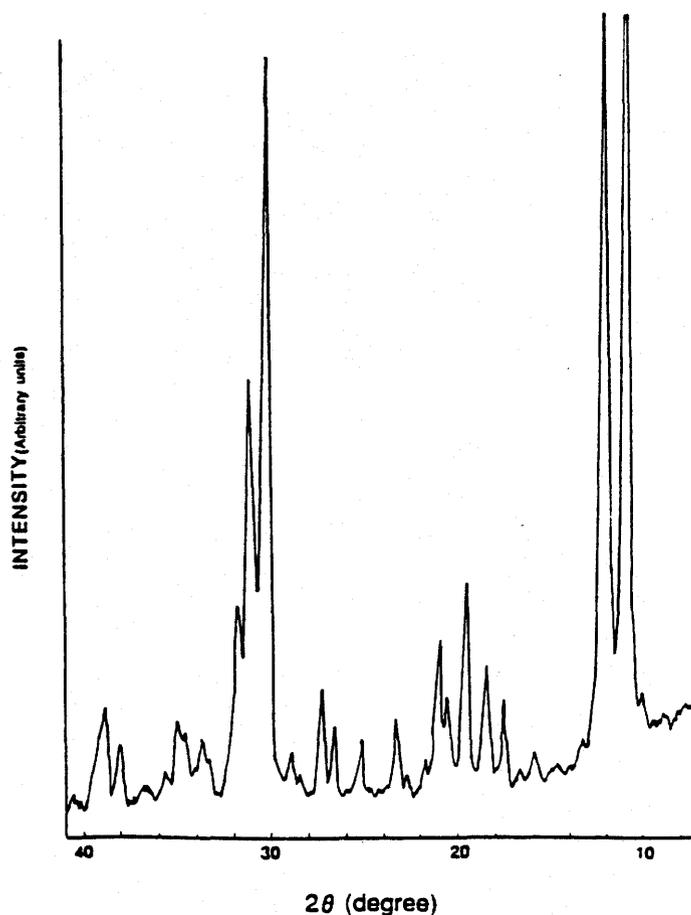


Figure 3.7 X-ray diffraction pattern of HZSM-5.

Table 3.5
Important physical and chemical data for HZSM-5

| | | | | | |
|---|--|----------------------------|------|------|------|
| BET Surface Area m^2/g | Pore Size, A° | Silica to Alumina Ratio | | | |
| 329 | 5.4 | 56 | | | |
| Maximum pore Volume, cc/g | Micropore Surface Area, m^2/g | | | | |
| 0.157 | 318.5 | | | | |
| <u>X-ray diffraction data</u> | | | | | |
| d(A) | I | d(A) | I | d(A) | I |
| 11.0 | 67.5 | 6.0 | 22.0 | 3.71 | 30.0 |
| 9.93 | 49.0 | 5.6 | 16.5 | 3.0 | 10.0 |
| 6.7 | 15.0 | 4.2 | 13.5 | 2.98 | 11.5 |
| 6.3 | 17.0 | 3.84 | 45.0 | | |

Table 3.6
Important physical and chemical data for H-mordenite

| | | | | | |
|---|--|----------------------------|-----|------|----|
| BET Surface Area m^2/g | Pore Size, A° | Silica to Alumina Ratio | | | |
| 112.6 | 6.4 | 14 | | | |
| Maximum Pore Volume, cc/g | Micropore Surface Area, m^2/g | | | | |
| 0.043 | 104.5 | | | | |
| <u>X-ray diffraction data</u> | | | | | |
| d(A) | I | d(A) | I | d(A) | I |
| 13.5 | 42 | 4.0 | 102 | 2.5 | 20 |
| 10.2 | 7 | 3.8 | 5 | 2.1 | 9 |
| 9.0 | 98 | 3.7 | 9 | 2.0 | 6 |
| 6.6 | 5 | 3.5 | 15 | 1.9 | 6 |
| 6.5 | 9 | 3.4 | 24 | 1.8 | 13 |
| 6.2 | 37 | 3.3 | 45 | | |
| 5.6 | 30 | 3.2 | 24 | | |
| 4.5 | 40 | 2.1 | 35 | | |
| 4.2 | 8 | 2.9 | 12 | | |
| 4.1 | 8 | 2.6 | 35 | | |

Table 3.7

Important physical and chemical data for H-Y

| | | | | | |
|---------------------------------------|--|----------------------------|----|------|----|
| BET Surface Area m ² /g | Pore Size, A ^o | Silica to Alumina Ratio | | | |
| 119.1 | 8.4 | 6.0 | | | |
| Maximum Pore Volume, cc/g | Micropore Surface Area, m ² /g | | | | |
| 0.016 | 103.5 | | | | |
| <u>X-ray diffraction data</u> | | | | | |
| d(A) | I | d(A) | I | d(A) | I |
| 14.0 | 102 | 3.3 | 37 | 2.3 | 13 |
| 8.8 | 8 | 3.1 | 8 | 2.1 | 10 |
| 7.0 | 30 | 3.0 | 16 | 1.7 | 13 |
| 5.0 | 40 | 2.9 | 21 | 1.6 | 13 |
| 4.2 | 23 | 2.8 | 48 | | |
| 4.0 | 31 | 2.6 | 20 | | |
| 3.5 | 47 | 2.5 | 19 | | |

Table 3.8

Important physical and chemical data for silicalite

| | | | |
|---------------------------------------|--|------|----|
| BET Surface Area m ² /g | Pore Size, A ^o | | |
| 401.9 | 5.4 | | |
| Pore Volume cc/g | Micropore Surface Area, m ² /g | | |
| 0.146 | 382.3 | | |
| <u>X-ray diffraction data</u> | | | |
| d(A) | I | d(A) | I |
| 11.0 | 100 | 4.0 | 63 |
| 10.0 | 66 | 3.8 | 30 |
| 9.5 | 20 | 3.7 | 20 |
| 6.5 | 12 | 3.6 | 30 |
| 6.0 | 16 | 3.2 | 15 |
| 5.5 | 9 | 3.0 | 10 |

4. RESULTS AND DISCUSSION

In this chapter, the results obtained under each phase of the research program are presented and discussed.

4.1 PHASE 1: CHARACTERIZATION AND STABILITY ANALYSIS OF WOOD-OIL

In this section, the results and discussions on phase 1 of the research program are presented. It consists of characterization of the wood-oil produced by the HPL of aspen poplar wood and its stability behaviour in the presence and absence of tetralin.

4.1.1 Distillation Characteristics of the Fresh Wood-oil

The intent of this work was to use vacuum distillation at different temperatures to characterize the wood oil. The results (presented in Table 4.1) show that the amounts of organic distillate increased from 21 wt.% at 85 °C to 62 wt.% at 200 °C before decreasing to 43 wt.% at 250 °C at 172 Pa. The amount of residue decreased with an increase in temperature to a minimum of 37 wt.% at 200 °C. The increase in the amount of residue above 200 °C may be due to polymerization of some components as reported by Sharma and Bakhshi [1991a]. Also, Molton et al. [1978] have shown that bio-oils are characteristically unstable to light, air and temperature changes and have the tendency to easily polymerize

Table 4.1
Distillation characteristics of fresh wood-oil showing the amount
and composition of distillate at different temperatures, wt.%.

| Pressure, 172 Pa | | | | | | | | | | |
|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Temp., °C | 85 | 115 | 140 | 165 | 175 | 190 | 200 | 220 | 250 | |
| <u>Distillation characteristics</u> | | | | | | | | | | |
| Distillate | 21.0 | 22.5 | 30.0 | 35.0 | 38.5 | 47.0 | 62.3 | 52.6 | 43.5 | |
| Residue | 79.0 | 77.5 | 70.0 | 65.0 | 61.5 | 53.0 | 37.7 | 47.4 | 56.5 | |
| Total | 100.0 |
| <u>Distillate composition</u> | | | | | | | | | | |
| Acids and Esters | 4.3 | 4.4 | 3.7 | 2.8 | 2.6 | 2.5 | 2.5 | 2.5 | 2.3 | |
| Alcohols | 7.2 | 10.3 | 8.6 | 3.8 | 3.5 | 3.6 | 6.6 | 5.3 | 5.2 | |
| Aldehydes and ketones | 9.1 | 11.0 | 9.0 | 12.4 | 14.2 | 10.0 | 7.8 | 7.7 | 7.5 | |
| Aliphatic hydrocarbons | 11.1 | 10.3 | 7.6 | 6.5 | 6.4 | 6.0 | 5.5 | 5.5 | 5.5 | |
| Aromatic hydrocarbons | 19.2 | 20.8 | 21.8 | 23.8 | 23.7 | 23.7 | 21.6 | 21.3 | 21.1 | |
| Ethers | 4.9 | 6.2 | 5.4 | 3.1 | 3.8 | 3.5 | 2.5 | 2.6 | 2.5 | |
| Furans | 4.0 | 4.0 | 3.8 | 2.2 | 3.0 | 3.2 | 3.4 | 3.4 | 3.6 | |
| Naphthenes | 9.2 | 9.8 | 12.4 | 13.0 | 13.7 | 12.1 | 12.1 | 12.0 | 11.9 | |
| Phenols | 12.6 | 11.0 | 16.8 | 19.0 | 21.4 | 24.7 | 28.1 | 29.8 | 35.2 | |
| Unidentified fraction | 18.5 | 12.3 | 10.1 | 13.3 | 7.7 | 11.7 | 9.9 | 9.8 | 4.9 | |
| Total | 100.0 |

when subjected to these conditions

Composition of Distillate Fraction from Fresh Wood-oil

The GC analyses of the distillate are presented in Table 4.1 and detailed compositions are given in Appendix D.1. The analysis indicated that the organic distillate was composed of a large number of oxygenated compounds and some hydrocarbons. The oxygenated compounds included acids, cyclic alcohols, aliphatic alcohols, aldehydes, cyclic ketones, substituted furans, ethers and alkyl substituted and alkoxy phenols. The hydrocarbons consisted of aromatic, polycyclic and long chain unsaturated hydrocarbons. About 80 individual compounds were identified by GC/MS and by use of pure compounds. The distillate contained 19-23 wt.% aromatic hydrocarbons, 11-35 wt.% phenols, 9-13 wt.% naphthenes, 5-11 wt.% aliphatic hydrocarbons, 7-14 wt.% aldehydes and ketones and 3-10 wt.% alcohols. The concentrations of acids, ethers and furans were in the range 2-6 wt.% each. Between 7-18 wt.% of the distillate could not be identified.

The phenolic fraction consisted mainly of phenol, guaiacol, p-cresol, p- and o-guaiacol, isoeugenol and catechol. The acids consisted mainly of formic acid, acetic acid and propionic acid. Similar components have been reported by other workers on HPL [Sharma and Bakhshi, 1991]] and pyrolytic oils [Soltes and Lin, 1987; Elliot et al., 1988]. Compounds such as aromatics, phenols and their alkyl

substituted fractions also have been reported as products from dry distillation of lignin [Goheen, 1971] and wood pyrolysis [Graef et al., 1981].

The mechanism of formation of these compounds from wood is still not well understood. However, various attempts have been made through the use of liquefaction of wood model compounds in order to understand the mechanism. For instance, Molton et al. [1978] used the liquefaction of cellulosic fraction of wood in an attempt to explain the formation of wood liquefaction products. It was suggested that in alkaline solutions glucose units are first "scissored" off the end of cellulose chains and then rearrange by reverse aldol type reaction into saccharinic acids. Further reactions yield aldehydes and ketones. Phenols are formed by dehydrogenation or oxidation of cyclohexanone derivatives which were formed from cyclization of terminally unsaturated pentanal and hexanal molecules. The formation of furans and its derivatives took place through the cyclization of diketones formed from simple aldehydes and ketones using aldol-type condensations. In general, it appears from the literature, that the liquefaction products are formed through an initial base-catalyzed decomposition or degradation (depolymerization) of the wood macromolecules [Forsskahl, 1978; Molton et al., 1978; Boocock et al., 1980] into C₂ to C₄ fragments followed by recombination and probably cyclization, partly via base-catalyzed aldol condensation, to liquefaction products.

Behaviour of Wood-oil Volatile Components with Distillation Temperature

The amount of total oxygenates and hydrocarbons in the distillate followed a similar trend as the distillate fraction. They increased in quantity until the 200 °C temperature mark was reached and then decreased (Figure 4.1) with further increases in temperature. Again, this trend could be linked to the increased polymerization of some of the wood oil components beyond 200 °C. The concentrations with temperature of the various chemical groups followed different trends. With increase in temperature, the concentrations of acids, ethers, aliphatic hydrocarbons and alcohols decreased. On the other hand, the concentrations of aromatic hydrocarbons, aldehydes and ketones and naphthenes reached maximum values around 175 °C (Table 4.1). Interestingly, the phenolic fraction continuously increased with temperature. The individual concentrations of major components at 175, 200 and 250°C are given in Table 4.2. It can be seen that with the exception of eugenol whose concentration increased to about 28 wt% of the distillate fraction at 250 °C, the concentrations of most components were below 2 wt% and changed with temperature.

These results have shown that the wood-oil was a complex mixture of acids, alcohols, aldehydes and ketones, aromatic and aliphatic hydrocarbons, ethers, esters, furans, naphthenes and phenols. It also contained a high non-volatile fraction.

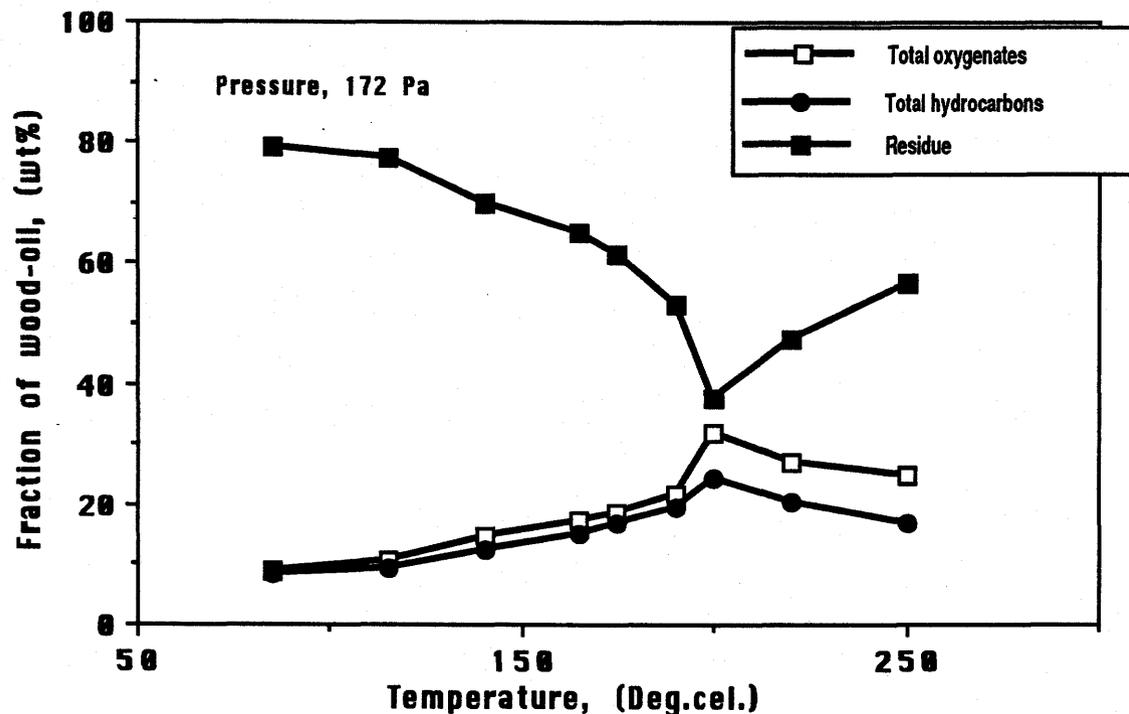


Figure 4.1 Relationship of temperature and composition of fresh wood-oil.

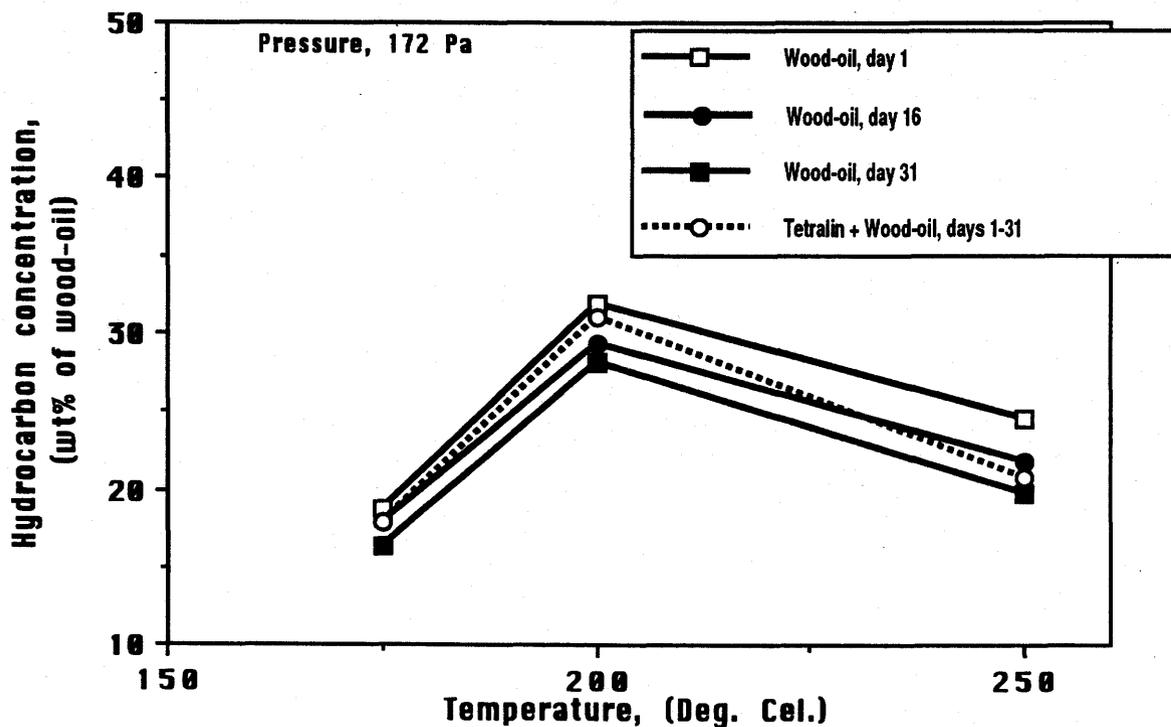


Figure 4.2 Relationship of temperature and total hydrocarbon concentration in wood oil at different storage times.

Table 4.2

Variation in the concentration of most abundant components of wood-oil distillate with temperature and storage time, wt.%.
 Pressure, 172 Pa.

| Time, days Temp., °C | ----- 1 ----- | | | ----- 16 ----- | | | ----- 31 ----- | | |
|--|---------------|------|------|----------------|------|------|----------------|------|------|
| | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 |
| 3-Propanoic acid | - | - | - | 0.2 | 0.3 | 0.5 | 0.1 | 0.2 | 0.1 |
| Cyclopentanol, 2-methyl- | 0.3 | 0.9 | 2.1 | 0.1 | 0.3 | 0.9 | - | - | - |
| Cyclohexanol,1-methyl- 4-(1-methylethenyl)- | - | - | - | 0.9 | 1.1 | 0.9 | 0.6 | 0.7 | 0.6 |
| Cyclopentanone, 2-methyl- | 3.1 | 1.3 | 1.1 | 1.7 | 1.0 | 0.4 | - | - | - |
| Benzene, (1-ethyl- 2-methyl-)- | - | - | - | 2.9 | 2.4 | 1.9 | 3.6 | 3.0 | 2.5 |
| Benzene, 2-butenyl- | 4.3 | 3.8 | 3.6 | 3.4 | 2.1 | 2.0 | 1.7 | 1.8 | 1.7 |
| Cyclooctadiene, 1,5-dimethyl- | 1.5 | 1.2 | 1.1 | 0.8 | 0.2 | - | 0.8 | 0.3 | - |
| Phenol | 2.6 | 1.9 | 1.6 | 0.8 | 0.4 | 0.3 | 0.4 | 0.3 | 0.3 |
| Phenol, 4-methyl- | 4.0 | 1.6 | 1.9 | 0.7 | 0.6 | 0.4 | 0.7 | 0.6 | 0.3 |
| Phenol, 2-methoxy -4-(2-propenyl-) | 5.9 | 23.0 | 28.3 | 14.5 | 17.1 | 19.5 | 12.4 | 16.8 | 18.6 |

The concentration of these fractions showed a complex relationship with temperature.

4.1.2 Stability Analysis of the Wood-oil

As mentioned earlier, the wood-oil stability was studied by observing the changes in some of its physical properties, distillation characteristics and composition with time. The results presented in Table 4.3 show that the viscosity of the wood-oil increased with time. A high viscosity implies poor flow characteristics. The density of the wood-oil remained unchanged. The amount of organic distillate at 175 °C decreased from 38 wt.% for the fresh wood-oil to 32 wt.% after 31 days. Similar decreases were observed at 200 and 250 °C. The decrease in distillate amount with time led to an increase in the amount of residue. The increase in the residue and viscosity suggests that polymerization-type reactions may have occurred in the wood-oil during its storage resulting in the formation of compounds with high molecular weight.

The compositions of the distillates obtained on days 1, 16 and 31 are given in Table 4.3 and also are plotted in Figures 4.2 and 4.3. The figures indicate that both the total oxygenates and hydrocarbon fractions decreased with time. The concentrations of aromatic hydrocarbons and phenols decreased while the concentration of aldehydes and ketones increased.

Table 4.3

Effect of storage time on the amount and composition of distillate from wood-oil at different temperatures, wt.%.
 Pressure, 172 Pa.

| Time, days | ----- 1 ----- | | | ----- 16 ----- | | | ----- 31 ----- | | |
|---|-----------------|-------|-------|-----------------|-------|-------|-----------------|-------|-------|
| Temp., °C | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 |
| <u>Viscosity and density of the wood-oil at 25 °C</u> | | | | | | | | | |
| Viscosity, Pa.s x 10 ³ | ----- 313 ----- | | | ----- 320 ----- | | | ----- 323 ----- | | |
| Density, kg.m ⁻³ | 1000 | | | 1000 | | | 1000 | | |
| <u>Distillation characteristics</u> | | | | | | | | | |
| Distillate | 38.5 | 62.3 | 43.5 | 36.0 | 54.1 | 38.3 | 32.4 | 51.0 | 33.4 |
| Residue | 61.5 | 37.7 | 56.5 | 64.0 | 45.9 | 61.7 | 67.6 | 49.0 | 66.6 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| <u>Distillate composition</u> | | | | | | | | | |
| Acids and Esters | 2.6 | 2.5 | 2.3 | 2.5 | 2.6 | 2.0 | 2.1 | 1.9 | 1.8 |
| Alcohols | 3.5 | 6.6 | 5.2 | 3.2 | 5.8 | 5.2 | 2.8 | 4.7 | 4.5 |
| Aldehydes and ketones | 14.2 | 7.8 | 7.5 | 14.8 | 11.5 | 11.1 | 16.8 | 14.0 | 13.8 |
| Aliphatic hydrocarbons | 6.4 | 5.5 | 5.5 | 6.0 | 5.1 | 5.1 | 5.6 | 4.8 | 4.7 |
| Aromatic hydrocarbons | 23.7 | 21.6 | 21.1 | 21.0 | 20.0 | 20.1 | 20.1 | 18.6 | 18.3 |
| Ethers | 3.8 | 2.5 | 2.9 | 5.6 | 4.8 | 6.1 | 6.6 | 5.1 | 6.2 |
| Furans | 3.0 | 3.4 | 3.6 | 3.2 | 3.3 | 3.5 | 3.0 | 3.6 | 3.7 |
| Naphthenes | 13.7 | 12.1 | 11.9 | 15.1 | 12.9 | 11.8 | 15.8 | 12.6 | 11.4 |
| Phenolics | 21.4 | 28.1 | 35.2 | 20.2 | 26.4 | 29.0 | 19.0 | 25.8 | 29.4 |
| Unidentified fraction | 7.7 | 9.9 | 4.9 | 8.4 | 7.6 | 6.1 | 8.2 | 8.9 | 6.2 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

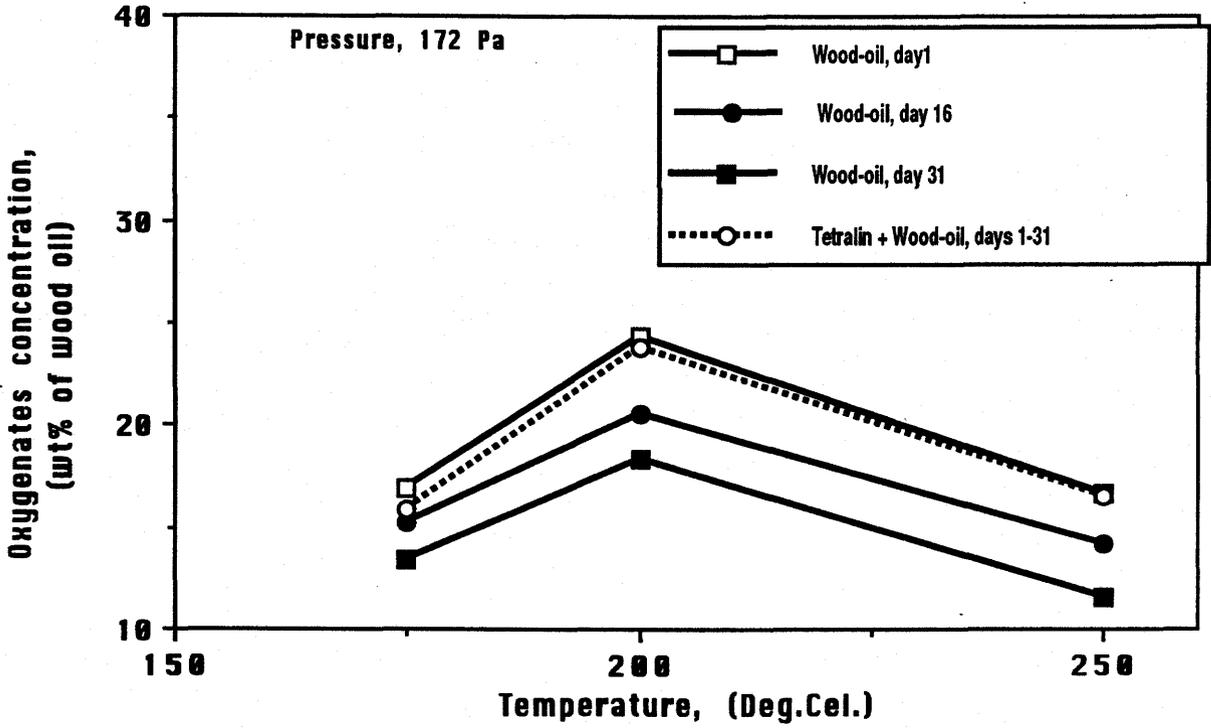


Figure 4.3 Relationship of temperature and total oxygenates concentration in wood-oil at different storage times.

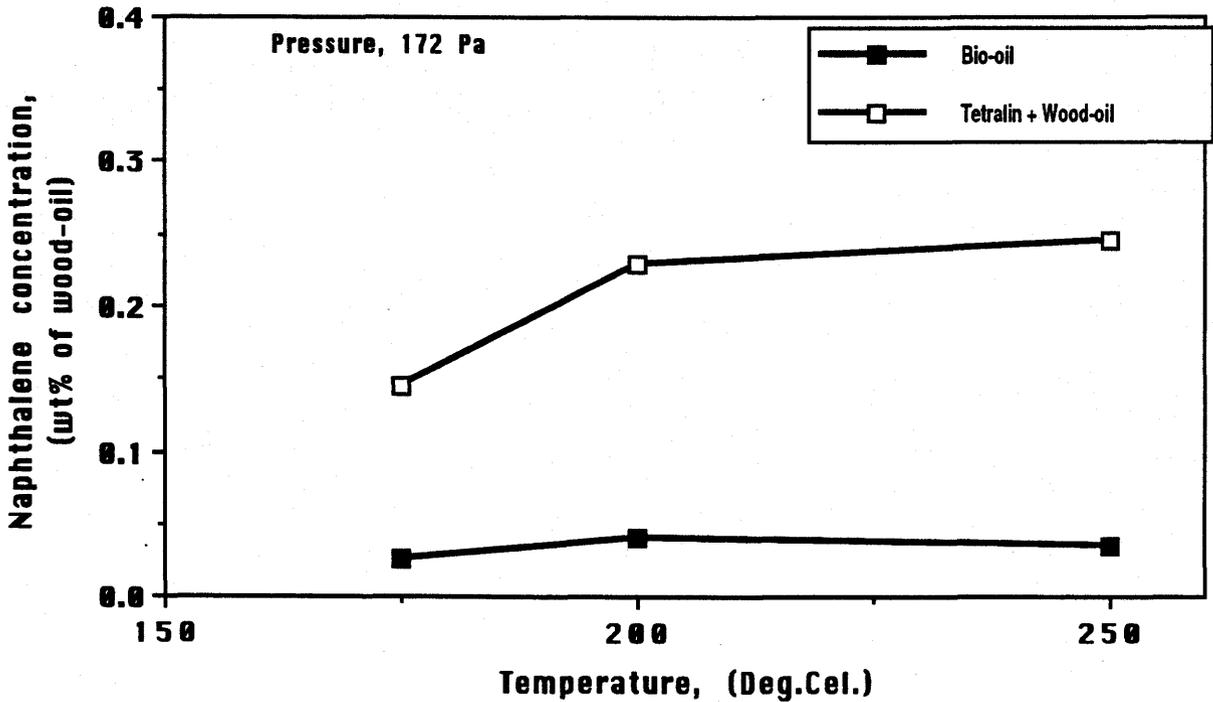


Figure 4.4 Relationship of temperature and naphthalene concentration in wood-oil and feed (wood-oil + tetralin).

Acids, alcohols, furans and aliphatic hydrocarbons were unchanged. The concentrations of the individual components in the distillate at different times, given in Table 4.2 and Appendix D.1 indicate that some components of the wood-oil reacted to form products which were not identified in the fresh distillate fraction. For instance, the concentration of 2-methyl cyclopentanol, 2-ethyl cyclopentanone, 2-butenyl-benzene, 1,5-dimethyl cyclooctadiene, phenol, 4-methyl phenol and 2-methoxy -4,2- propenyl phenol decreased. This may suggest involvement of these components in polymerization-type reactions. Other compounds such as 1-methylpropyl ester of formic acid, 1- methyl -4-(1- methyl ethenyl) cyclohexanol and ethyl-2-methyl-benzene which were not present in significant amounts in the fresh wood-oil distillate increased during storage.

The elemental analyses of various fractions of the wood-oil are presented in Table 4.4. The analyses show that the oxygen content of the distillate at 175 °C decreased from 22.7 wt.% on day 1 to 18.8 wt.% on day 31. The oxygen content of the residue increased from 16.3 wt.% on day 1 to 21.9 wt.% on day 31 while its carbon content decreased from 75.6 wt.% to 71.1 wt.% in the same period also suggesting a continuous reactivity of the wood-oil components during storage.

These results suggest that the wood-oil was unstable with time, and that these reactions occurred as a result of the tendency to achieve stability.

Table 4.4

Effect of storage time on the elemental analyses of distillate and residue fractions at different temperatures, wt.%

| Pressure, 172 Pa. | | | | | | |
|--|---------------|------------|------------|------------|------------|--|
| Time, days | ----- 1 ----- | | | 16 | 31 | |
| Temperature, °C | 175 | 200 | 250 | 200 | 200 | |
| <u>Wood-oil</u> | | | | | | |
| Distillate | | | | | | |
| C | 68.4 | 67.7 | 67.7 | 67.9 | 70.7 | |
| H | 9.2 | 9.6 | 10.8 | 10.5 | 10.5 | |
| N | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | |
| O | 22.4 | 22.7 | 21.5 | 21.6 | 18.8 | |
| Residue | | | | | | |
| C | 75.6 | 76.3 | 73.9 | 73.9 | 71.1 | |
| H | 8.1 | 7.8 | 6.7 | 7.7 | 7.0 | |
| N | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | |
| O | 16.3 | 15.9 | 19.4 | 18.4 | 21.9 | |
| <u>Feed (wood-oil + tetralin)</u> | | | | | | |
| Distillate | | | | | | |
| C | 76.8 | 71.4 | 71.9 | 72.2 | 71.9 | |
| H | 8.3 | 8.9 | 8.7 | 8.6 | 8.3 | |
| N | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | |
| O | 14.9 | 19.7 | 19.4 | 19.2 | 19.8 | |
| Residue | | | | | | |
| C | 78.4 | 82.4 | 82.6 | 82.4 | 82.2 | |
| H | 8.3 | 7.2 | 7.1 | 7.4 | 7.4 | |
| N | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | |
| O | 13.3 | 10.4 | 10.3 | 10.2 | 10.4 | |

Determined by difference.

The unstable behaviour of bio-oils in general have been explained by either oxidative coupling mechanism involving free radicals produced during the liquefaction stage or by an ionic mechanism [Molton et al., 1978; Zinkel, 1977]. Molton et al. [1978] reports the polymerization of oils produced from the liquefaction of cellulosic wastes. It was observed that the oil was stable until it was exposed to air, when polymerization began. The polymerization was assumed to be the normal one of oxidative coupling involving free radicals. Also, Zinkel [1977] reports the coagulation (polymerization) of the components of tall oil with shelf life and suggested polymerization through oxidative coupling of the unsaturated components was responsible.

4.1.3 Mechanism of Wood-oil Instability

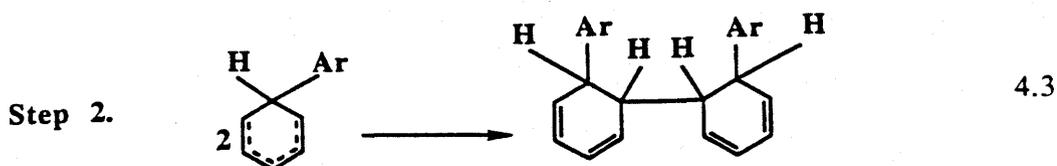
The above results indicated that the wood-oil was unstable and its properties changed with time. The poor stability probably may be due to oxidation/polymerization reactions which occurred during storage. Since the wood-oil was produced by thermochemical conversion of wood powder at high pressure (5 MPa) and temperature (360°C), these severe conditions may have induced cleavage of bonds in the biomass leading to free radical formation [Soltes and Lin, 1987]. The normal C-C bond energy is about 380 KJ/mol and thermal excitation of molecules becomes sufficient to break these bonds at temperatures of 350-550°C. In addition, certain bonds

are exceptionally weak (especially O-O bonds) and therefore can break at lower temperatures. Compounds with such bonds can initiate radical processes at 50-150°C [Pryor, 1966]. Similar results have been hypothesized for coal pyrolysis and liquefaction [Bockrath, 1983; McMillen et al., 1987]. As a result, in the absence of a stabilizing agent such as a good hydrogen-donor solvent, secondary substitution and radical combination reactions (polymerization reactions) may have occurred during storage leading to high molecular weight products.

March [1977] discussed coupling reactions involving free radicals of aromatic nature. Based on March's development, a mechanism based on aromatic substrate substitutions involving coupling of the aromatic rings is suggested to explain the polymerization of the aromatic components. According to this mechanism, aromatic free radicals, Ar^{\cdot} , are first produced by bond cleavage at the liquefaction stage. If ArH is another aromatic ring, the possible overall reaction is,



The first step of the polymerization process may involve the radical attacking the ring as in reaction 4.2 which may terminate by simple coupling leading to the formation of a higher molecular weight compound as in reaction 4.3.



Since reactions involving free radicals are slow at room temperature [Taylor and Battersky, 1967], the increase in the residue and viscosity of the wood-oil with time was also slow.

Generally, it has been considered that phenolate radicals give stable molecular products by coupling in pairs [Taylor and Battersky, 1967]. The rate of disappearance of these radicals has been shown to follow second order kinetics, thus demonstrating coupling or dimerization as shown by reaction 4.4.



Further reactions could take place to form polymeric products. These reactions may be slow, especially when there is steric hindrance. In wood-oils, which have high molecular weights and long or large molecules, the effect of steric hindrance may be enormous, thus leading to slow polymerization reactions involving the phenolate molecules.

4.1.4 Stability Analysis of Wood-oil + Tetralin Mixture

As has been stated earlier, tetralin was added to the wood-oil since it was intended to upgrade the wood-oil with tetralin in order to lower coke formation and possibly improve the stability of the oil. As a result, the effect of tetralin addition on wood-oil viscosity, density, chemical composition and distillation characteristics was investigated from day 1 to 31. The results were calculated on a tetralin-free basis and are presented in Table 4.5. The results indicated that viscosity, density and composition of the wood-oil remained almost unchanged over these days. The concentrations of the hydrocarbons and oxygenates also remained almost unchanged over this period as shown in Figures 4.2 and 4.3.

A comparison of the distillation characteristics of fresh wood-oil (Table 4.3) and fresh feed (Table 4.5) showed that some changes in the wood-oil properties occurred when tetralin was added to the wood-oil. As expected, the viscosity decreased and also there was a slight decrease in the amount of distillate. The composition of the distillate also changed slightly (Tables 4.3 and 4.5). For instance, the concentrations of acids, alcohols and aliphatic hydrocarbons in the feed were higher and the concentrations of naphthenes and phenols were lower than those in the wood-oil. Fractions of furans, ethers, aromatic hydrocarbons and aldehydes and ketones were unchanged.

Table 4.5
Effect of storage time on the amount and composition of distillate
from feed (wood-oil + tetralin), wt.%.

| Pressure, 172 Pa | ----- 1 ----- | | | ----- 16 ----- | | | ----- 31 ----- | | |
|---|---------------|-------|-------|----------------|-------|-------|----------------|-------|-------|
| Time, days | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 |
| Temp., °C | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 |
| <u>Viscosity and density of the feed at 25 °C</u> | | | | | | | | | |
| Viscosity, Pa.s x 10 ³ | ----- | 26 | ----- | ----- | 26 | ----- | ----- | 26 | ----- |
| Density, kg.m ⁻³ | | 985 | | 985 | | 985 | | 985 | |
| <u>Distillation characteristics</u> | | | | | | | | | |
| Distillate | 36.4 | 59.4 | 43.4 | 36.1 | 59.0 | 42.9 | 36.7 | 50.2 | 42.7 |
| Residue | 63.6 | 40.6 | 56.6 | 63.9 | 41.0 | 57.1 | 63.3 | 40.8 | 57.3 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| <u>Distillate composition</u> | | | | | | | | | |
| Acids and Esters | 5.3 | 5.5 | 5.0 | 6.0 | 5.3 | 4.9 | 5.8 | 5.3 | 4.9 |
| Alcohols | 7.7 | 6.9 | 4.3 | 8.0 | 7.1 | 4.2 | 7.9 | 7.1 | 4.6 |
| Aldehydes and Ketones | 10.0 | 9.1 | 8.1 | 9.7 | 9.3 | 8.4 | 9.3 | 9.2 | 8.4 |
| Aliphatic Hydrocarbons | 8.7 | 8.6 | 8.7 | 8.6 | 9.0 | 8.8 | 9.0 | 9.0 | 8.9 |
| Aromatic Hydrocarbons | 24.6 | 20.8 | 18.7 | 24.2 | 21.0 | 19.0 | 24.4 | 20.6 | 19.1 |
| Ethers | 2.4 | 3.1 | 3.6 | 2.4 | 3.4 | 3.6 | 2.1 | 3.3 | 3.6 |
| Furans | 3.5 | 3.8 | 1.7 | 3.6 | 4.0 | 1.6 | 3.2 | 3.9 | 1.8 |
| Naphthenes | 10.1 | 10.6 | 10.6 | 10.1 | 10.4 | 10.8 | 10.3 | 10.6 | 11.0 |
| Phenolics | 19.7 | 23.8 | 25.1 | 19.4 | 24.0 | 25.0 | 20.0 | 24.3 | 25.6 |
| Unidentified fraction | 7.3 | 7.8 | 14.2 | 7.8 | 6.5 | 13.7 | 7.5 | 6.7 | 12.1 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

The elemental analyses of the distillate and residue fractions from the wood-oil-tetralin feed mixture are presented in Table 4.4. It can be seen that the oxygen, carbon and hydrogen contents of the residue fraction did not change with time. These results indicate that the addition of tetralin as a hydrogen-donor solvent helped to improve the stability of the wood-oil and also lowered its viscosity.

4.1.5 Role of Tetralin and Mechanism for Wood-oil Stabilization

Since the wood-oils are hydrogen deficient, the addition of hydrogen may be carried out under pressure by addition of gaseous hydrogen using a hydrogenating catalyst or by using a hydrogen-donor solvent which supplies hydrogen through dehydrogenation reactions. The dehydrogenation of tetralin to naphthalene liberates hydrogen radicals according to reaction 4.5. Each molecule of tetralin can provide a maximum of 4 hydrogen radicals.

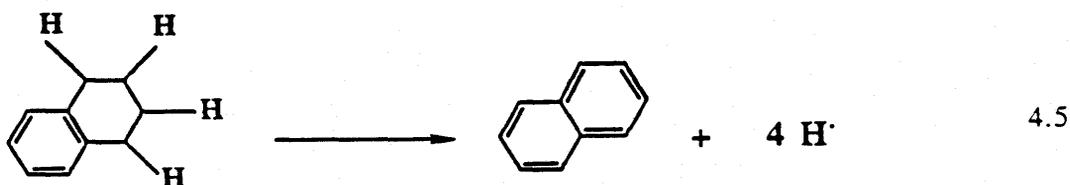
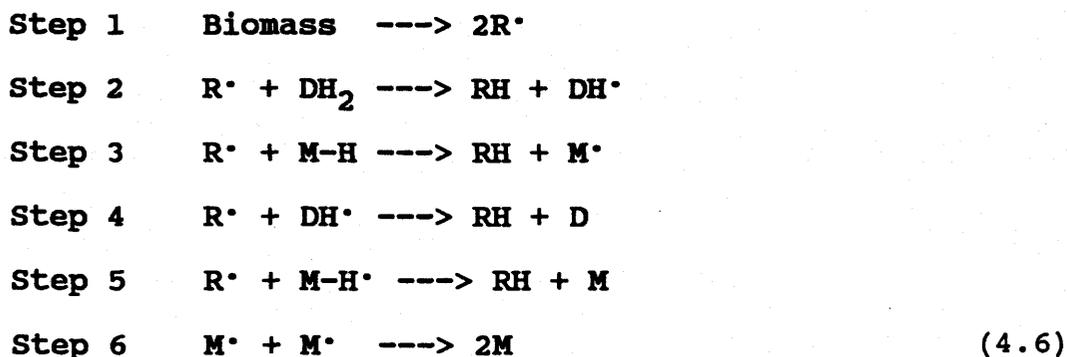


Figure 4.4 shows that the concentration of naphthalene in the wood-oil-tetralin feed increased about six times (0.03-0.04 to 0.15-0.25 wt%) from that in the wood-oil due to tetralin dehydrogenation. Based on these observations, the apparent

stability of the wood-oil in the presence of tetralin may be explained on the basis of free radical reactions and the hydrogen-donor properties of tetralin, similar to those described by Bockrath [1983] and McMillen et al. [1987] for coal liquefaction.

According to the postulated mechanism represented by reaction 4.6, the dissociation of some bonds in the biomass generates two free radicals, R^\cdot (step 1) which can abstract hydrogen in two ways; from the donor solvent, DH_2 (step 2), or some wood-oil component, M (step 3). As a result of further dehydrogenation of the solvent (step 4) or some part of the wood-oil component (step 5), the fragments from the fractured bond are stabilized.



Furthermore, the free radicals produced from step 3 also may combine in step 6 to form high molecular weight fraction. But as observed experimentally, this step occurs to a very small extent.

The results from the above work have shown that the wood-

oil was characteristically unstable. However, its stability improved when it was mixed with tetralin. The apparent instability and stability was explained by free radical mechanisms.

4.2. PHASES 2 AND 3: UPGRADING OF WOOD OIL IN THE PRESENCE AND ABSENCE OF STEAM

In this section, the major objective was to study the viability of converting the high molecular weight wood-oil to fuel range hydrocarbon products and useful chemicals and also to study the advantages of using steam as co-feed. It includes results and discussions on the upgrading of the wood-oil in the presence and absence of steam, effect of catalyst regeneration and upgrading of wood-oil volatile fraction.

4.2.1 Non-catalytic Upgrading (Blank Runs)

In these runs the wood-oil was thermally treated in the presence and absence of steam over inert berl saddles with the objective of determining the extent of upgrading. In addition, the sensitivity of wood-oil to heat in the presence and absence of steam was studied. These studies also allowed a comparison to be made between the two processes, i.e. thermal treatment with and without steam, and between non-catalytic and catalytic processing of the wood-oil.

The products from these runs consisted of a carbonaceous deposit (coke or char), gas, residue and organic liquid product (organic distillate). The mass balances at various temperatures are presented in Table 4.6. As can be seen, the organic distillate was a maximum 49.3 wt% at 330 °C when processing in the absence of steam, and 45.5 wt% at 410 °C

Table 4.6

Effect of temperature on overall product distribution (wt% of wood-oil fed) and yield of hydrocarbons from non-catalytic (blank runs) upgrading of wood-oil in the presence and absence of steam.

Overall product distribution

| | | Temperature, °C | | | |
|----------------------|-----|-----------------|-------|-------|-------|
| | | 290 | 330 | 370 | 410 |
| Carbonaceous Deposit | N.S | 8.0 | 8.1 | 13.6 | 20.4 |
| | S | 4.7 | 5.0 | 8.6 | 12.5 |
| Gas | N.S | 1.6 | 2.0 | 2.8 | 4.0 |
| | S | --- | T | T | 0.1 |
| Organic Distillate | N.S | 44.0 | 49.3 | 47.7 | 41.8 |
| | S | 37.4 | 41.7 | 43.7 | 45.5 |
| Residue | N.S | 45.2 | 39.8 | 34.7 | 32.8 |
| | S | 56.0 | 51.7 | 46.1 | 40.1 |
| Unaccounted | N.S | 1.2 | 0.8 | 1.2 | 1.0 |
| | S | 1.8 | 1.6 | 1.6 | 1.8 |
| Total | N.S | 100.0 | 100.0 | 100.0 | 100.0 |
| | S | 100.0 | 100.0 | 100.0 | 100.0 |

Yields of Hydrocarbons

| Hydrocarbon | | Temperature, °C | | | |
|-----------------------|-----|-----------------|------|------|------|
| | | 290 | 330 | 370 | 410 |
| Aromatics | N.S | 14.5 | 17.1 | 14.5 | 11.5 |
| | S | 10.4 | 12.1 | 10.2 | 10.4 |
| Cyclic aliphatics | N.S | 4.8 | 4.4 | 2.8 | 2.5 |
| | S | 3.7 | 4.5 | 4.3 | 5.4 |
| Non-cyclic aliphatics | N.S | 3.3 | 3.9 | 3.7 | 2.1 |
| | S | 2.9 | 3.2 | 3.4 | 4.0 |
| Total | N.S | 22.6 | 25.4 | 21.0 | 16.1 |
| | S | 17.0 | 19.8 | 17.9 | 19.8 |

NS -- Processing without steam

S -- Processing with steam

when processing in the presence of steam.

In both cases, the carbonaceous deposit and gas products increased monotonically with temperature. However, the fractions of these products were lower when processing in the presence of steam. The residue fraction decreased with temperature increase and was higher at all temperatures when processing in the presence of steam.

Hydrocarbon Formation

Analysis of the distillate product showed that it contained a number of single and polycyclic aromatics (such alkyl derivatives of phenanthrene and naphthalene) cyclic hydrocarbons (naphthenes) and non-cyclic aliphatic hydrocarbons which were formed probably from thermal cracking [Chen et al., 1989]. The effect of temperature on the yield of these hydrocarbons is also presented in Table 4.6. A maximum of 19.8 wt% and 25.4 wt% hydrocarbons at 330 °C were measured in the presence and absence of steam, respectively. Also, the yield of aromatics was a maximum at 12.1 and 17.1 wt% at 330 °C when processing in the presence and absence of steam, respectively. The hydrocarbon fraction consisted of a number of C₆ to C₁₅ aromatics and aliphatics. The effect of temperature on the yield of major hydrocarbons is shown in Appendix D.2. As can be seen, these hydrocarbon compounds fall within either the gasoline boiling point range (C₅ to C₁₂, 30-210 °C) or kerosene boiling point range (C₉ to C₁₅, 149-260

°C) [Probstein and Hicks, 1982].

A comparison of the two processes show higher hydrocarbon yields for upgrading in the absence of steam than in the case when upgrading was carried out in the presence of steam. Lower retention of the wood-oil molecules during co-processing with steam probably resulted in the lower hydrocarbon formation.

The sensitivity of the oil to heat can be seen in the extent to which it produces a carbonaceous deposit. This is higher in the absence of steam (8.0 to 20.4 wt%) than in the presence of steam (4.7 to 12.5 wt%) showing that the tendency to polymerize is less profound in the presence of steam. It has been mentioned [Churin et al., 1990] that bio-oils are thermally unstable and easily polymerize at high temperatures due to the presence of free radicals present in them or generated by some of the oxygenates upon heating. This implies that ways should be found to minimize coking or charring during processing of wood-oils. In some upgrading work [Baker and Elliot, 1988], attempts have been made to lower the charring by first processing the wood-oil at a lower temperature to stabilize it before processing at high temperatures.

The high fraction of residue resulting from upgrading in the presence of steam may probably imply lower cracking rates when processing in the presence of steam compared to when processing without steam. Since cracking is essential to hydrocarbon formation, the lower yield of hydrocarbons

resulting from upgrading with steam appears to confirm the lower cracking rates. Lower retention times of wood-oil molecules during upgrading with steam may have resulted in the high residue fraction since contact times are critical for the cracking of molecules.

In this work it has been shown that thermal treatment of the wood-oil alone resulted in the formation of about 20 and 25 wt% hydrocarbon products when processing with and without steam, respectively. However, these fractions were low and the distillate product was still highly oxygenated since conversion to fuel range hydrocarbons was the major objective. Between 32-37 wt% (with steam) and 40-42 wt% (without steam) oxygenated compounds were identified in the distillate product. Also, high amounts of residue (between 32.7 and 56.0 wt%) and up to 20 wt% coke were obtained. These results imply that further processing or an alternative processing route was required to upgrade the wood-oil.

4.2.2 Catalytic Upgrading

Following the thermal treatment runs it became evident that to further reduce the high residue fractions alongside obtaining high quality hydrocarbon products it was necessary to use a catalyst during the processing of the wood oil. In these experiments, HZSM-5 was used for this purpose. The proven performance of HZSM-5 catalyst to deoxygenate and crack various feeds has already been mentioned in chapters 2 and 3.

4.2.2.1 Tetralin Reactivity Measurements

Since the wood-oil was processed together with tetralin, preliminary experiments were carried out to determine the conversion of tetralin by HZSM-5 in the temperature range studied. A summary of these results are presented in Table 4.7. As can be seen, tetralin was essentially non-reactive below 370 °C. Above 370 °C, conversions were up to 4 and 6 % at 410 °C for processing in the presence and absence of steam, respectively. In both processes, the main products were benzene, toluene and xylenes.

The effect of tetralin conversions on the products from upgrading the wood-oil-tetralin mixture were later taken into account.

4.2.2.2 Overall Product Distribution

The products from catalytically treating the wood-oil over HZSM-5 catalyst included an aqueous fraction, coke, gas, organic liquid product (i.e. organic distillate), residue and unconverted wood-oil (tar). Tables 4.8 and 4.9 show the effect of process time (run time) and temperature, respectively, on the yields of these products.

Table 4.7

Tetralin reactivity and extent of tetralin dehydrogenation before and after catalytic upgrading of wood-oil over various catalysts.

| Temperature, °C | Silicalite | | | H-mordenite | | |
|--------------------|------------|-------|-------|-------------|-------|-------|
| | 330 | 370 | 410 | 330 | 370 | 410 |
| Conversion | 2.8 | 4.1 | 7.0 | --- | 0.8 | 1.9 |
| ¹ N/T | 0.003 | 0.005 | 0.005 | --- | 0.004 | 0.006 |
| ² N/T | 0.005 | 0.008 | 0.006 | --- | 0.006 | 0.009 |

| Temperature, °C | H-Y | | | Silica-alumina | | |
|--------------------|-------|-------|-------|----------------|-------|-------|
| | 330 | 370 | 410 | 330 | 370 | 410 |
| Conversion | --- | 1.0 | 2.2 | --- | 0.4 | 0.9 |
| ¹ N/T | --- | 0.004 | 0.004 | --- | 0.001 | 0.003 |
| ² N/T | 0.001 | 0.006 | 0.007 | 0.002 | 0.003 | 0.003 |

| Temperature, °C | HZSM-5 (With steam) | | | HZSM-5 (No steam) | | |
|--------------------|---------------------|-------|-------|-------------------|-------|-------|
| | 330 | 370 | 410 | 330 | 370 | 410 |
| Conversion | --- | 1.5 | 4.2 | --- | 1.7 | 6.0 |
| ¹ N/T | 0.001 | 0.002 | 0.002 | 0.002 | 0.003 | 0.004 |
| ² N/T | 0.003 | 0.004 | 0.004 | 0.005 | 0.007 | 0.009 |

¹ Naphthalene to tetralin ratio for reaction of tetralin feed only over catalysts.

² Naphthalene to tetralin ratio for tetralin reactivity after co-processing with wood-oil.

4.2.2.3 Effect of Process Time (Run Time)

These runs were carried out in order to study the effect of length of experimental run, i.e., process time, on the yield and selectivity of desired products, i.e., the organic distillate and its hydrocarbon content. Information from these runs aided in selecting the process time that provided optimum yields and selectivities of the desired product. It was also important to determine when to terminate the experimental runs. Since the organic distillate was the main product of interest, it was essential that the run time selected should provide an optimum yield of this product as well as optimum hydrocarbon yield and selectivity. The effect of process time on each product (mass balances) are presented in Table 4.8. The results show that optimum organic distillate yields of 57.6 and 64.9 wt% were obtained at a run time of 30 min in both processes.

Effect of Process Time on Hydrocarbon Yield

The composition of the organic distillate was predominantly hydrocarbons and phenols. Alcohols, aldehydes and ketones, and furans were also identified in relatively smaller fractions (Appendix D.3). Of major interest was the hydrocarbon content of the organic distillate. The various hydrocarbons identified consisted of aromatics, and cyclic and non-cyclic aliphatics. The effect of process time on the yield

Table 4.8

Effect of process time on the overall product distribution from upgrading wood-oil over HZSM-5 in the presence and absence of steam at 370 °C.

| Product | | Run time, min | | | |
|----------------------|-----|---------------|-------|-------|-------|
| | | 15 | 30 | 45 | 60 |
| Aqueous Fraction | N.S | T | 2.8 | 2.1 | 2.2 |
| | S | 2.9 | 2.8 | 2.8 | 2.3 |
| Coke | N.S | 17.1 | 9.9 | 12.9 | 13.1 |
| | S | 4.0 | 4.3 | 5.1 | 6.1 |
| Gas | N.S | 7.3 | 4.4 | 4.0 | 4.0 |
| | S | 5.8 | 3.0 | 2.5 | 2.3 |
| Organic Distillate | N.S | 49.7 | 57.6 | 56.7 | 44.4 |
| | S | 64.5 | 64.9 | 62.0 | 60.5 |
| Residue | N.S | 16.6 | 18.3 | 18.2 | 31.2 |
| | S | 17.7 | 21.9 | 22.0 | 23.4 |
| Unconverted Wood-oil | N.S | 4.2 | 4.7 | 4.8 | 4.9 |
| | S | --- | --- | 2.7 | 2.9 |
| Unaccounted | N.S | 4.7 | 2.3 | 2.9 | 2.0 |
| | S | 2.8 | 1.9 | 1.9 | 1.7 |
| Total | N.S | 100.0 | 100.0 | 100.0 | 100.0 |
| | S | 100.0 | 100.0 | 100.0 | 100.0 |

of the hydrocarbons for the two processes are shown in Figures 4.5 and 4.6. It can be seen that during processing in the absence of steam, the yield of aromatic hydrocarbons reached an optimum value of 37 wt% at 30 min. However, in the presence of steam, the yield decreased progressively from 37.8 wt% at 15 min to 32.4 wt% at 60 min. A similar trend was shown by total hydrocarbon yield.

The hydrocarbon fraction consisted of high concentrations of benzene, toluene, and xylenes and alkylated benzenes within the gasoline boiling point range (Appendix D.3). The yield of these compounds were also affected by the run time. These compounds may have been formed from a number of reactions including cracking, deoxygenation and aromatizations, such as, hydrogen and hydride transfer and cyclization [Prasad and Bakhshi, 1986]. Isomerization and alkylation reactions of benzene may have led to the formation of xylene and other alkyl substituted benzene derivatives. It has been reported [Prasad and Bakhshi, 1986; Chen et al., 1989] that the pore size and structure of HZSM-5 catalyst induce shape selectivity properties that enhance the isomerization of various di- and trimethyl substituted benzene derivatives.

Again it can be deduced that in order to achieve optimum yields of hydrocarbons, a 30 min run time should be employed when processing without steam. On the other hand, run times less than 30 min was appropriate when processing in the presence of steam. Also, it has been shown that the yield of

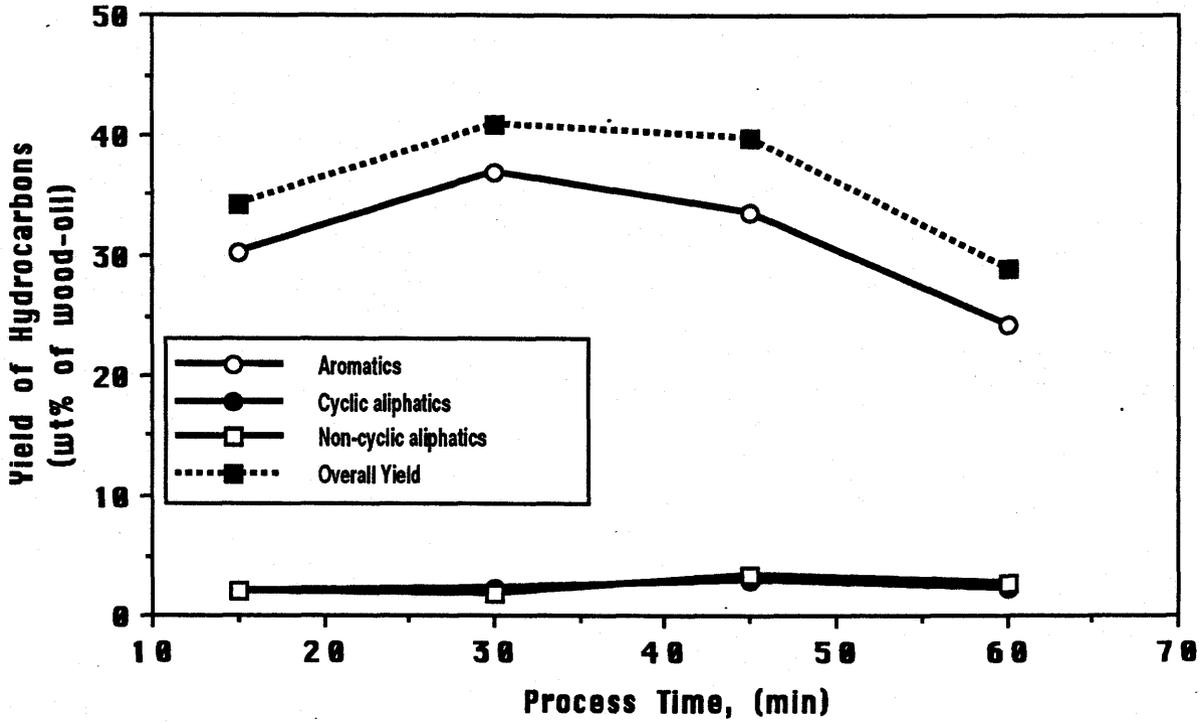


Figure 4.5 Effect of process time on the yield of various hydrocarbons (absence of steam).

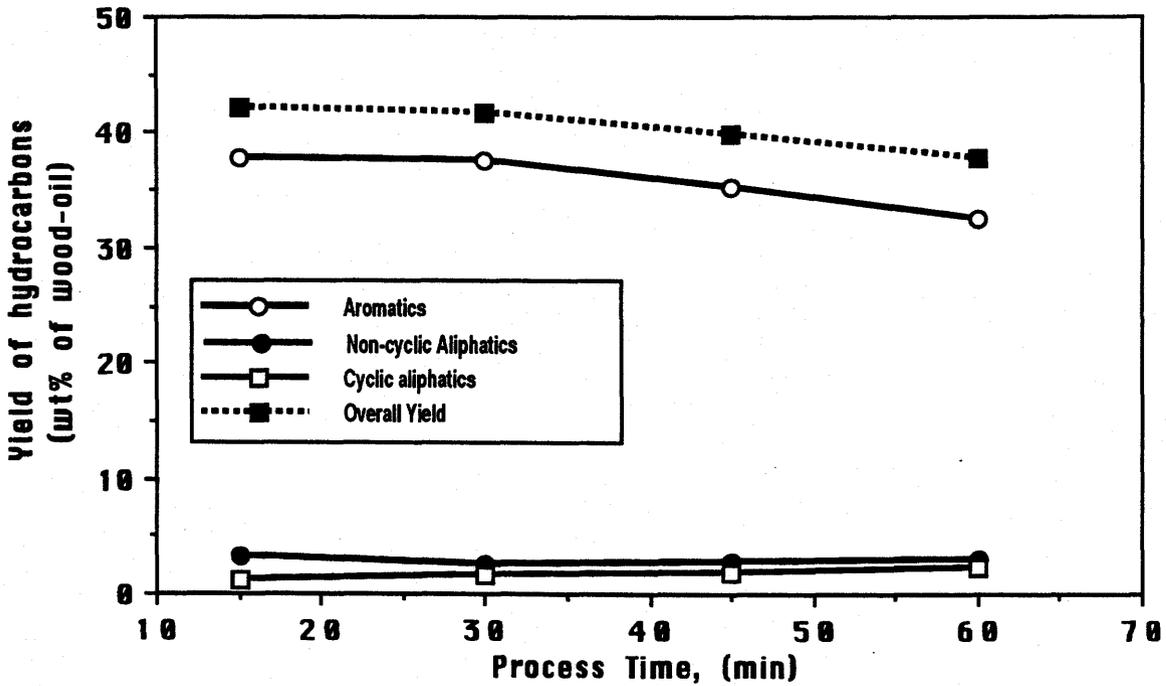


Figure 4.6 Effect of process time on the yield of hydrocarbons (presence of steam).

individual compounds were affected by the run time. Thus, the process time could be manipulated to achieve desired concentrations or yields of various compounds or products.

Effect of Process Time on Hydrocarbon Selectivity

Since the major objective of this work was the production of hydrocarbons, it was necessary to determine the yield of the hydrocarbon fraction (desired product) relative to the other products of upgrading (undesired product), i.e. selectivity. This kind of information could aid in determining and manipulating those conditions that could provide quality hydrocarbon fractions, in this case, the process time. In this section of the work, the effect of process time on the selectivity of hydrocarbons calculated by equation 4.1 was studied.

$$S = \frac{H(\text{wt}\%)}{(100 - H(\text{wt}\%) - UC(\text{wt}\%) - UA(\text{wt}\%))} \quad (4.1)$$

The results are plotted in Figures 4.7 and 4.8 for aromatic hydrocarbons and cyclic and non-cyclic aliphatic hydrocarbons. As can be seen, the overall hydrocarbon selectivity was an optimum of 0.79 at 30 min when processing without steam. For processing with steam, the selectivity decreased progressively from 0.77 at 15 min to 0.66 at 60 min.

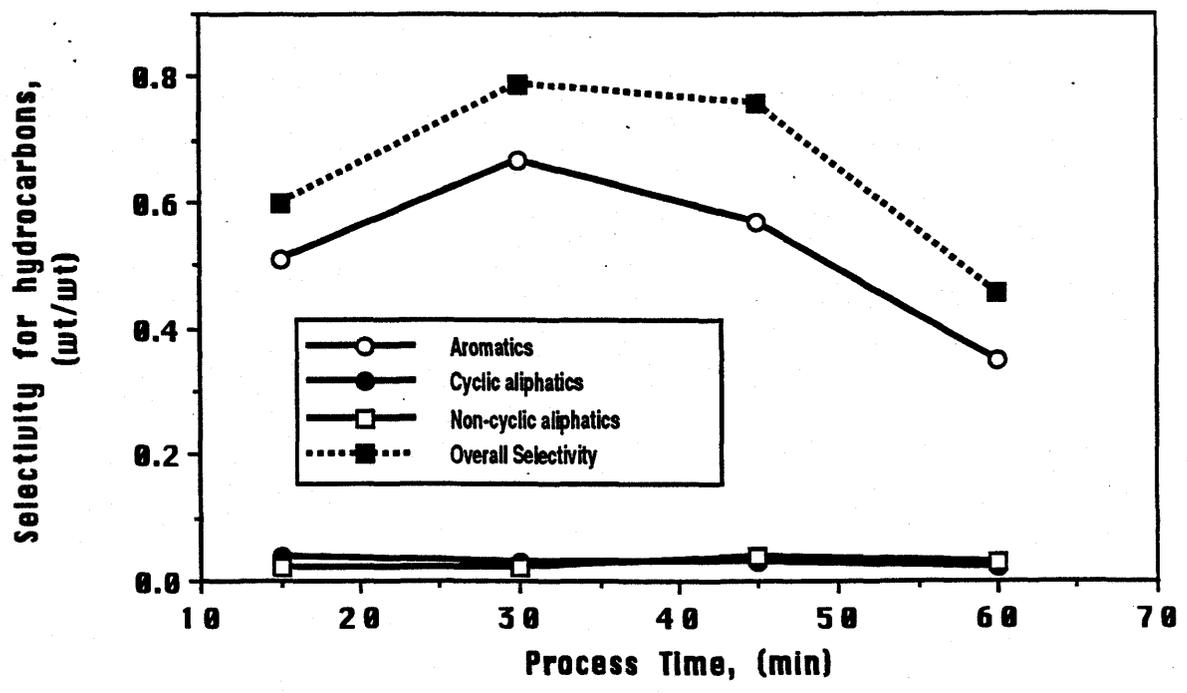


Figure 4.7 Effect of process time on the selectivity for hydrocarbons (absence of steam).

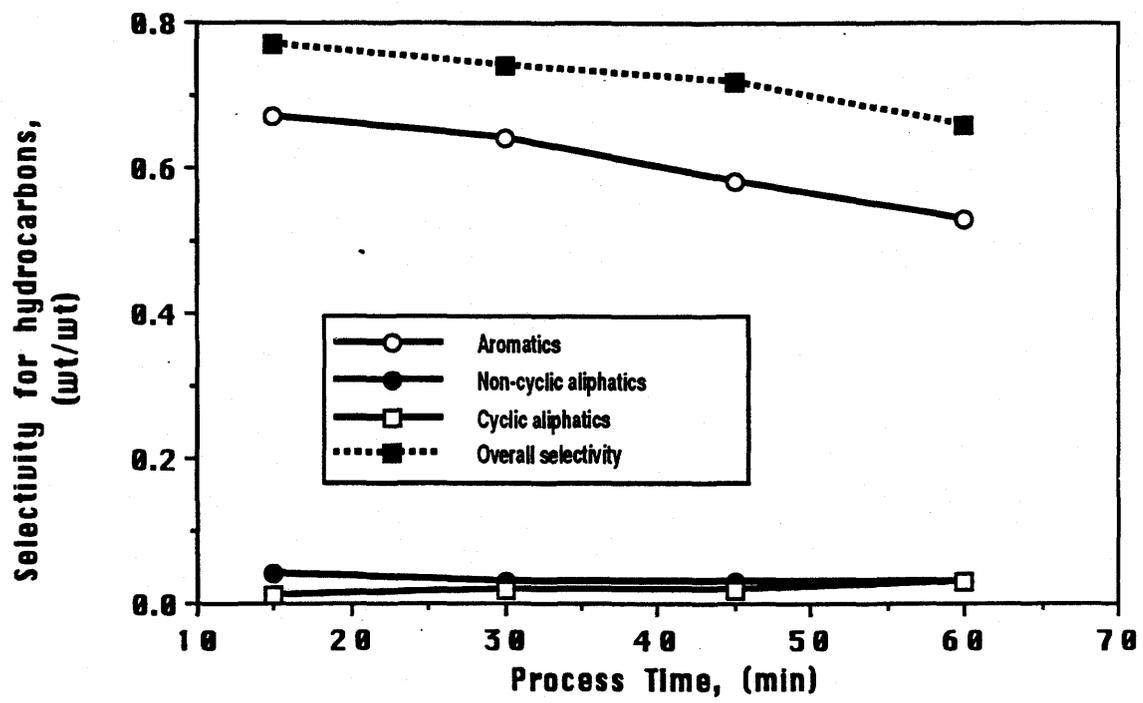


Figure 4.8 Effect of process time on the selectivity for hydrocarbons (presence of Steam).

These results (Figures 4.7 and 4.8) also show that the selectivity for aromatic hydrocarbons was significantly higher than the selectivity for aliphatic hydrocarbons in both processes. In the absence of steam the selectivity for aromatics was between 0.35 and 0.67 and for aliphatics, between 0.05 and 0.06. When processing in the presence of steam, the selectivity for aromatic hydrocarbons was between 0.53 and 0.67 and for aliphatic hydrocarbons, between 0.04 and 0.06. The high aromatic selectivity may have resulted from the shape selectivity property of the HZSM-5 catalyst. It has been mentioned [Probststein and Hicks, 1982; Prasad and Bakhshi, 1986; Chen et al., 1989] that the medium pore structure of the HZSM-5 catalyst enhances the selectivity of C_5 to C_{12} hydrocarbons of aromatic nature. Also, Weisz et al. [1979] mentioned that during the processing of bio-oils using zeolites, the molecules are first thermally cracked on the surface of the catalyst and subsequently restructured within the zeolite pores. This restructuring includes a dynamic folding of molecules within the pores resulting in enhanced aromatization of the molecules.

It has been shown in the process time studies that in the absence of steam, the yield and selectivity reached optimum values at 30 min. The lower values below 30 min were probably due to the high coke formation (Table 4.8). Beyond 30 min, the yield and selectivity decreased with process time probably due

to increasing unconverted wood-oil (tar) build-up and coverage of active sites by coke. Similarly, the progressive decrease in the yield and selectivity of hydrocarbons when processing in the presence of steam may be due to increased deposition of unconverted oil (tar) and coke build up with process time.

Chantal et al. [1984] also studied the effect of run time during the upgrading of a pyrolytic oil and observed that the tar fraction increased with the run time. The tars significantly contributed to the formation of coke leading to catalyst deactivation and significant reduction in the selectivity for hydrocarbons if they were allowed to stay on the catalyst. Thus, these results suggest that a combination of factors such as contact time of molecules with the active sites and the nature and number of the active sites available for reaction are vital in determining the yield and selectivity of hydrocarbons products.

In a summary, it has been shown that when upgrading without steam, a run time of 30 min was most favourable. On the other hand, run times of 30 min and below were most favourable when upgrading in the presence of steam. As a result, an experimental run of 30 min was employed in subsequent upgrading of the wood-oil at other reaction conditions.

Table 4.9
Effect of temperature on the overall product distribution from upgrading wood-oil over HZSM-5 in the presence and absence of steam.

| Product | | Temperature, °C | | | | |
|----------------------|-----|-----------------|-------|-------|-------|-------|
| | | 290 | 330 | 370 | 390 | 410 |
| Aqueous Fraction | N.S | 1.6 | 3.6 | 2.8 | 2.8 | 2.8 |
| | S | 0.8 | 1.2 | 2.0 | 3.3 | 3.5 |
| Coke | N.S | 1.2 | 4.4 | 6.3 | 9.9 | 12.3 |
| | S | 0.3 | 2.8 | 4.3 | 5.9 | 6.9 |
| Gas | N.S | 2.4 | 2.4 | 3.6 | 4.4 | 7.1 |
| | S | 0.8 | 1.2 | 2.4 | 3.8 | 6.3 |
| Organic Distillate | N.S | 43.1 | 46.5 | 55.6 | 58.3 | 57.1 |
| | S | 45.6 | 51.0 | 65.0 | 63.2 | 59.5 |
| Residue | N.S | 20.5 | 22.3 | 21.5 | 18.3 | 17.9 |
| | S | 29.2 | 27.9 | 22.0 | 21.9 | 21.7 |
| Unconverted Wood-oil | N.S | 28.4 | 19.3 | 8.3 | 4.7 | --- |
| | S | 21.8 | 14.6 | 2.8 | --- | --- |
| Unaccounted | N.S | 2.8 | 1.5 | 1.9 | 1.6 | 2.8 |
| | S | 1.5 | 1.3 | 1.5 | 1.9 | 2.1 |
| Total | N.S | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | S | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

4.2.2.4 Effect of Temperature During Catalytic Upgrading

The effect of temperature on the upgrading of the wood-oil are presented in Table 4.9 (mass balances). As can be seen, optimum organic distillate yields of 58 wt% at 390 °C (without steam) and 65 wt% at 370 °C (with steam) were obtained.

The coke and gas fractions increased monotonically with temperature indicating that these were probably end products of the reaction. Coke formation increased with temperature probably because of increased polymerization reactions of aromatics, non-volatile molecules of the wood-oil and oxidative coupling of oxygenated compounds such as phenols [Taylor and Battersky, 1967; Vasilakos and Austgen, 1985].

The optimum residue fraction was 22.3 wt% at 330 °C when processing in the absence of steam; with steam, the residue fraction decreased progressively with temperature from 29.2 wt% at 290 °C to 21.7 wt% at 410 °C. The general decrease in residue with temperature shows the extent to which the high molecular weight components of the wood-oil gets converted as the temperature was increased.

In these runs it can be seen that the reaction temperature was a critical factor in determining the product yields of upgrading.

Effect of Temperature on Hydrocarbon Yield

Since a major objective of this work was to optimize the yield of hydrocarbons, it was essential to study the effect of temperature on this fraction. Similar to the process-time studies, the hydrocarbons identified were composed of three main types: aromatics hydrocarbons, cyclic hydrocarbons and non-cyclic aliphatic hydrocarbons. The effect of temperature on these hydrocarbon products is shown in Figures 4.9 and 4.10. As can be seen, during upgrading in the absence of steam the yield increased from 30.2 wt% at 290 °C to 43.3 wt% at 390 °C before decreasing. For processing in the presence of steam, the yield increased from 24.6 wt% at 290 °C to 42.0 wt% at 370 °C before decreasing. The decrease beyond 370 and 390 °C may be due to enhanced polymerization of some of the aromatics hydrocarbons.

The detailed composition of the organic distillate is presented in Appendices D.4 (by chemical groups) and D.5 (by individual compounds). As can be seen, the organic distillate was highly aromatic in nature and the yields of each compound were strongly depended on temperature. Benzene, toluene, xylenes and other alkyl substituted derivatives of benzene were the major products. These compounds fall within the gasoline boiling point range. Also present were various oxygenated compounds comprising mainly phenols and small fractions of alcohols, aldehydes and ketones, and furans.

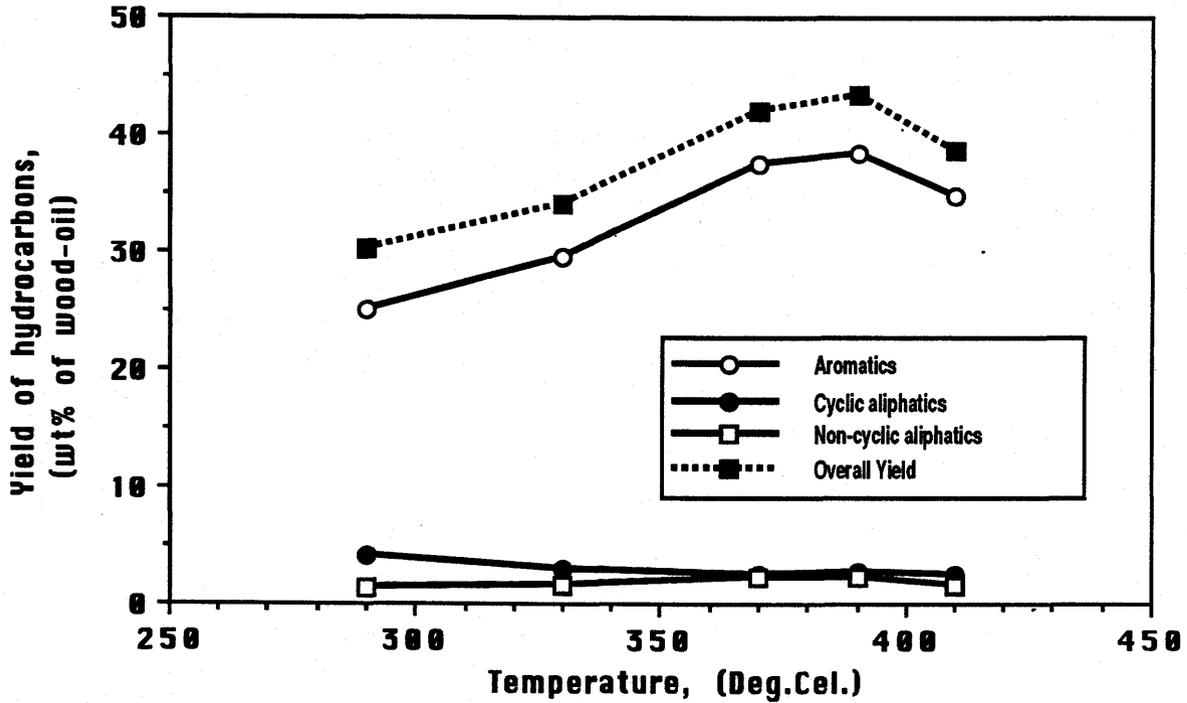


Figure 4.9 Effect of temperature on the yield of hydrocarbons (absence of steam).

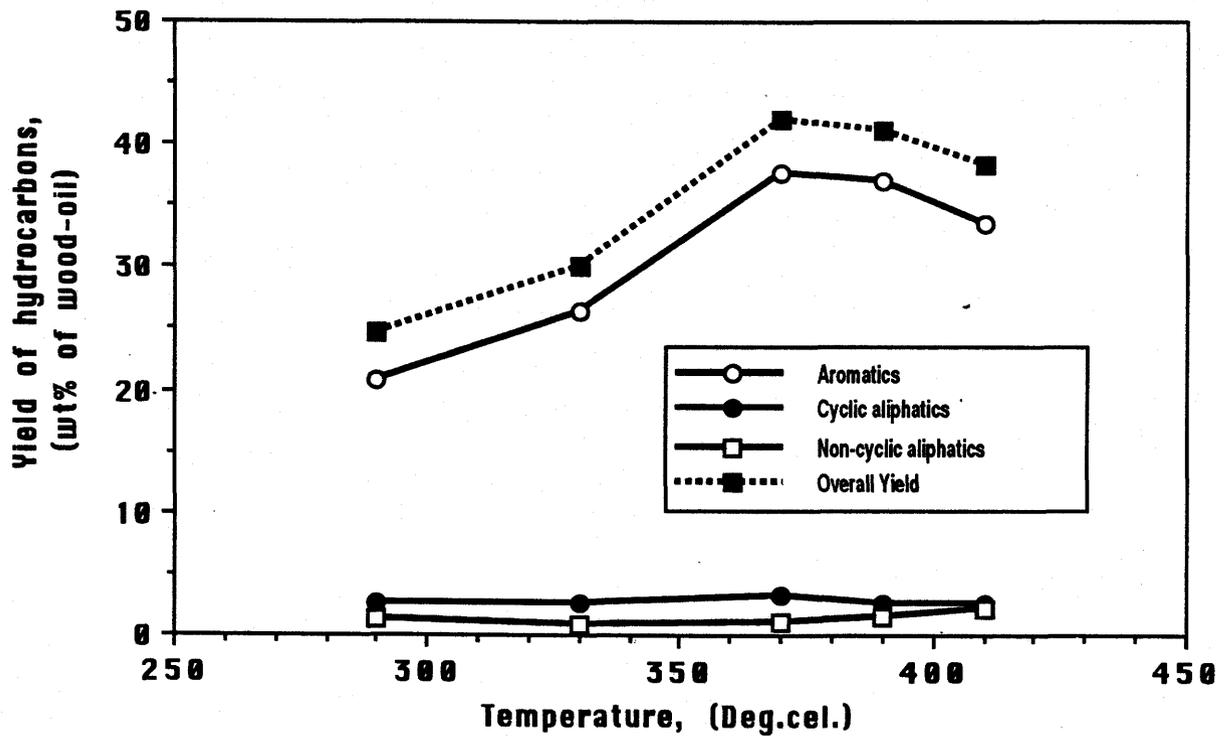


Figure 4.10 Effect of temperature on the yield of hydrocarbons (presence of Steam).

Chantal et al. [1984] observed a similar product distribution when a pyrolytic oil was contacted with HZSM-5 catalyst at temperatures of 330-450 °C. In their work, about 10-15 wt% of the oil was converted to C₅-C₁₀ hydrocarbons.

Effect of Temperature on Hydrocarbon Selectivity

As shown in Figures 4.11 and 4.12, the selectivity of the various hydrocarbons also varied with temperature. The selectivity with temperature followed a similar trend as the yield. Optimum selectivity was at 370 °C and was 0.88 and 0.78 when processing in the absence and presence of steam, respectively. Optimum aromatic selectivity was also obtained at 370 °C.

It has been mentioned earlier that the three-dimensional framework of the HZSM-5 was the origin of the enhanced selectivity for C₅ to C₁₂ hydrocarbons. Chen et al. [1989] also mentions that the operating temperature and pressure of the system influence the selectivity of compounds. This is because diffusion rates of molecules into and out of the pores of the catalyst depend on the temperature and pressure of the system. Generally, as the temperature is increased, the diffusion rates of molecules increase, thus enhancing subsequent reactions. Since the main reaction favours aromatic formation within the pores of the catalyst the selectivity values increase with increase in temperature. However, beyond 370 °C, polymerization

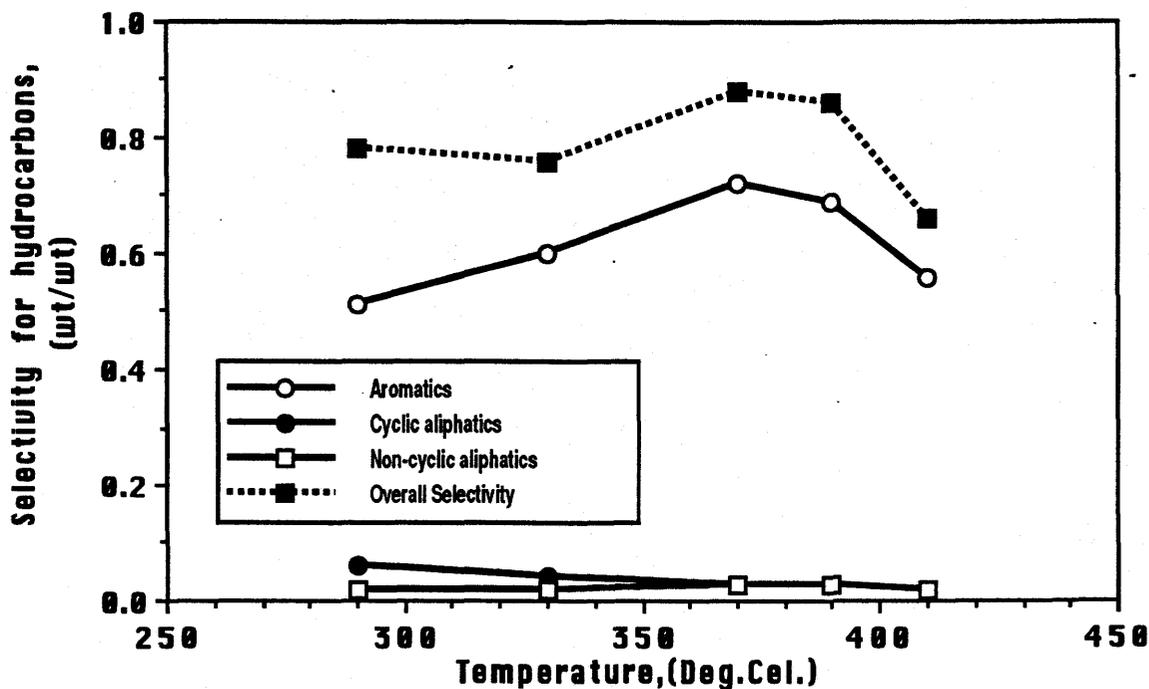


Figure 4.11 Effect of temperature on the selectivity for hydrocarbons (absence of steam).

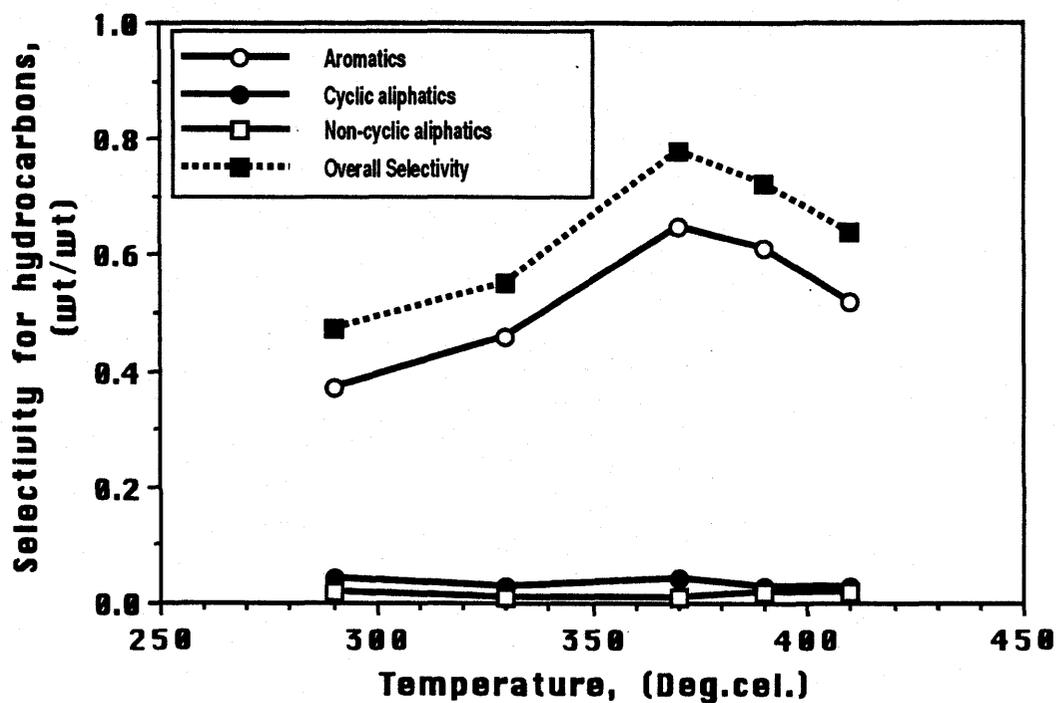


Figure 4.12 Effect of temperature on selectivity for hydrocarbons (presence of steam).

reactions become prominent so that there is a net decrease in the selectivity of aromatics and therefore hydrocarbons selectivity.

4.2.2.5 The Role of Steam

As observed above, a comparison of the two processes showed that processing with steam resulted in a higher organic distillate, lower coke formation and a lower hydrocarbon yield and selectivity. A similar result was reported by Prasad et al. [1986] when they processed canola oil in the presence of steam over HZSM-5 catalyst. Prasad et. al. [1986] and Ison and Gorte [1984] explained these observation on the basis of competitive adsorption between the steam and wood-oil molecules. It was mentioned that steam molecules were preferentially adsorbed on the active Bronsted acid sites so that these sites no longer existed as protons (H^+) instead of as hydronium ions (H_3O^+), thus, resulting in changes in the strength of the active sites. This in turn altered the rates of cracking, aromatization and polymerization reactions. In relation to this work, the presence of steam may have lowered the cracking of the non-volatile fraction and reduced aromatization reactions. Also, since some of the aromatic hydrocarbons polymerized to form coke, these results have shown that polymerization reactions may have also been reduced.

These results have shown that hydrocarbon-rich products of various concentrations could be produced from the catalytic upgrading of wood-oil. The yields and selectivities of the upgrading products were strongly dependent on temperature. Optimum values for hydrocarbon products were obtained at 370 °C and 390 °C when processing in the presence and absence of steam, respectively. Processing with steam resulted in increased yields of organic distillate, reduced coke formation and reduced hydrocarbon formation compared to processing without steam.

4.2.2.6 Effect of Catalyst Regeneration

Since catalyst performance in terms of its re-use capability is a vital part of catalytic processes, the HZSM-5 catalyst used in this work was tested for its performance by regenerating and re-using. In these runs the product distributions, yield and selectivity for hydrocarbons, BET surface area and x-ray diffraction measurements were monitored after each regeneration/re-use cycle.

The results after the fourth cycle are shown in Figures 13 and 14 for major products of interest. As can be seen during upgrading without steam, the organic distillate fraction decreased by 5.6 wt%, coke increased by 1.6 wt% and residue 1.5 wt%. Also, there was a decrease in the hydrocarbon content from 42.1 to 35.0 wt%. The BET surface area changed from 329 to 319 m²/g. When processing in the presence of

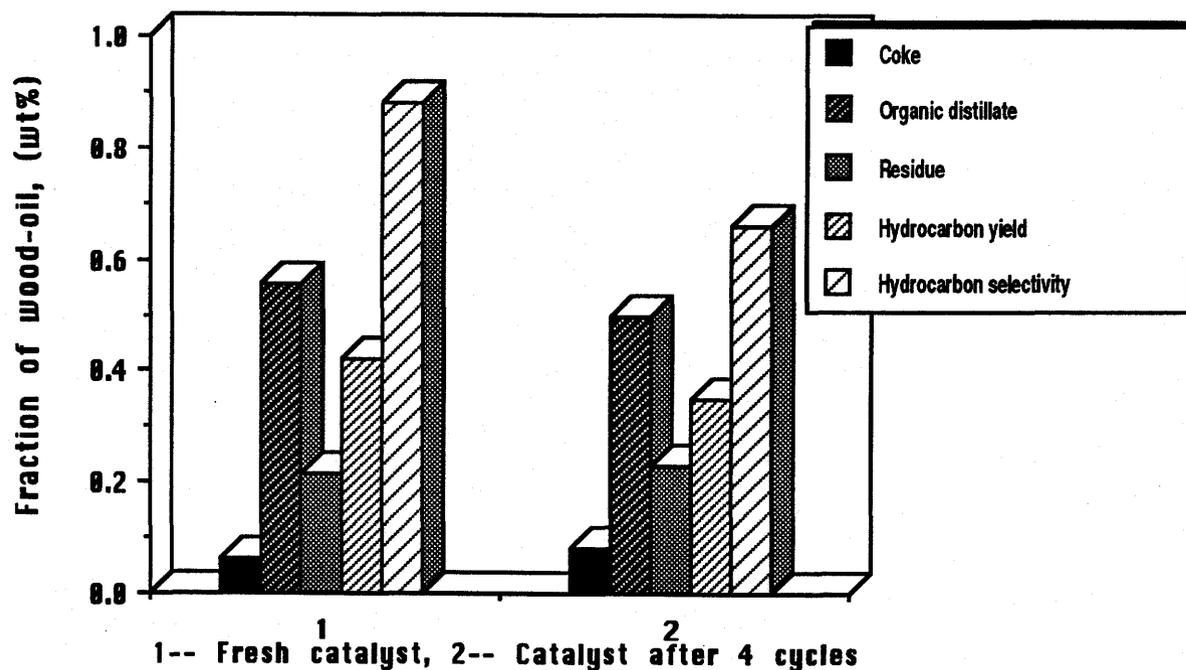


Figure 4.13 Effect of catalyst regeneration on the product distribution (absence of steam).

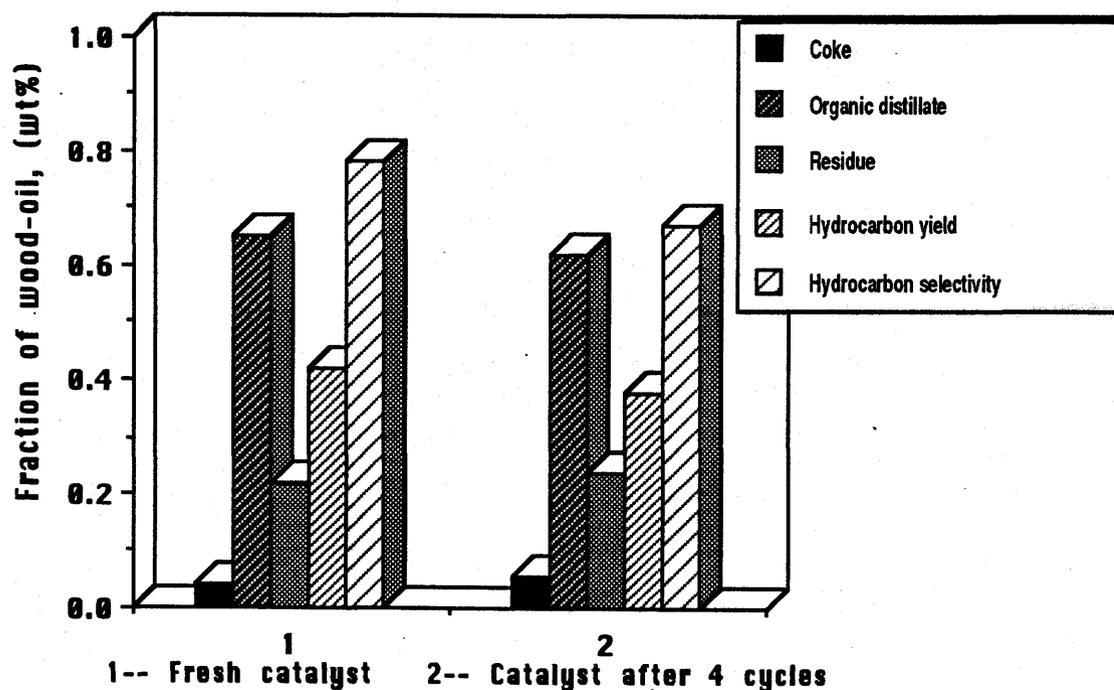


Figure 4.14 Effect of catalyst regeneration on the product distribution (presence of Steam).

steam, the organic distillate decreased by 3 wt%, coke increased by 1.1 wt%, residue increased by 1.6 wt. The yield and selectivity for hydrocarbons decreased by 4.2 wt% and 0.11, respectively. Also, the BET surface area changed to 321 m²/g. However, in both processes, the interplanar spacing, "d" values, obtained from x-ray diffraction analysis did not change indicating that the crystallinity of the catalyst was still maintained.

The decrease in BET surface area is not fully understood but may have resulted from changes in the available active surface area. Also, the changes in the yield of the various products and selectivity of hydrocarbons may have resulted from changes in either the acid strength, distribution or the number of available acid sites present on the catalyst after regeneration. Topsoe et al. [1981] have shown that the strength of acid sites decreased and also some acid sites disappeared when HZSM-5 catalysts were regenerated. Despite these changes it can be concluded that HZSM-5 was structurally stable under these conditions and that it could be regenerated and re-used with little change in its performance.

4.2.3 Upgrading of Wood-oil Volatile Fraction

Here, the volatile portion of the wood-oil obtained after vacuum distillation at 200 °C and 172 Pa was upgraded with HZSM-5 catalyst at 3.6 WHSV and a temperature range 330 to 410 °C. This was carried out without co-feeding steam. The

objective was to improve on the quality of the organic distillate.

The mass balances at each temperature are presented in Table 4.10. The products were, an aqueous fraction, coke, gas, organic distillate and residue fraction. As can be seen, the organic distillate fraction decreased with increase in temperature from 93.1 wt% at 330 °C to 72.5 wt% at 410 °C compared to upgrading of the whole wood-oil (between 46.1 and 58.3 wt%). This indicates that higher organic distillates can be produced after separation of the volatile fraction from the non-volatile fraction of the wood-oil.

The coke, gas and residue fraction increased progressively with temperature. The coke ranged between 2.0 and 9.7 wt% compared to 4.4 and 12.3 wt% when processing the whole wood-oil indicating that lower coke formation can be achieved when volatile fractions of the wood are processed separately from the non-volatiles. Also, no unconverted oils (tars) were produced at all the temperatures studied compared with 2.8 to 14.6 wt% produced when the whole wood-oil was processed. These imply that catalyst deactivation by combined effects of coke and tar were much lower when the wood-oil volatiles alone were processed. This means the catalysts could be used for much longer times than when the whole wood-oil was processed.

Table 4.10

Effect of temperature on overall product distribution, yield and selectivity of hydrocarbons from upgrading wood-oil volatiles over HZSM-5 catalyst.

Overall Product Distribution

| Product | Temperature, °C | | |
|----------------------|-----------------|-------|-------|
| | 330 | 370 | 410 |
| Aqueous fraction | T | 1.5 | 3.1 |
| Coke | 2.0 | 6.4 | 9.7 |
| Gas | 4.1 | 6.8 | 9.8 |
| Organic Distillate | 93.1 | 81.8 | 72.5 |
| Residue | T | 2.5 | 4.2 |
| Unconverted wood-oil | --- | --- | --- |
| Unaccounted | 0.8 | 0.9 | 0.7 |
| Total | 100.0 | 100.0 | 100.0 |

Yields and Selectivities of Hydrocarbons

| Hydrocarbon | | Temperature, °C | | |
|-----------------------|--------|-----------------|------|------|
| | | 330 | 370 | 410 |
| Aromatics | Yield | 44.3 | 50.3 | 51.3 |
| | Selec. | 0.80 | 1.03 | 1.05 |
| Cyclic aliphatics | Yield | --- | --- | --- |
| | Selec. | --- | --- | --- |
| Non-cyclic aliphatics | Yield | 3.4 | 2.3 | 1.7 |
| | Selec. | 0.04 | 0.02 | 0.02 |
| Total yield | | 47.7 | 52.6 | 52.7 |
| Overall selectivity | | 0.93 | 1.13 | 1.13 |

Effect of Temperature on Hydrocarbon Yield and Selectivity (Wood-oil Volatiles)

Analysis of the organic distillate showed that it was very rich in hydrocarbons. In Appendix D.6 the effect of temperature on the yield of the major hydrocarbons are presented. The hydrocarbons identified included mainly aromatics and non-cyclic aliphatics. No cyclic aliphatics were identified. It also contained large amounts of benzene, toluene, xylene and other alkylated benzenes within the gasoline boiling point range. The effect of temperature on the yield and selectivity of hydrocarbons are also shown in Figures 4.15 and 4.16. As can be seen, optimum yield and selectivity were obtained at 370 °C. Beyond 370 °C, no further increases were observed.

A comparison with the case when the whole wood-oil was processed shows that hydrocarbon yields between 44.3 to 51.3 wt% and selectivity between 0.93 and 1.13 were obtained when processing the wood-oil volatile alone compared to hydrocarbon yields of 34.1 and 43.3 wt% and selectivities of 0.66 and 0.88 when processing the whole wood-oil. A similar work was performed by Mathews et al. [1985] by contacting different boiling point fractions of a wood-oil with HZSM-5 catalyst using hydrogen as carrier gas. In this case, the wood-oil was preheated and the fractions vaporizing between 30-150, 150-215, 215-275, and 275-390 °C were fed to a reactor maintained at 350-650 °C. The highest conversion to C₆ to C₁₀

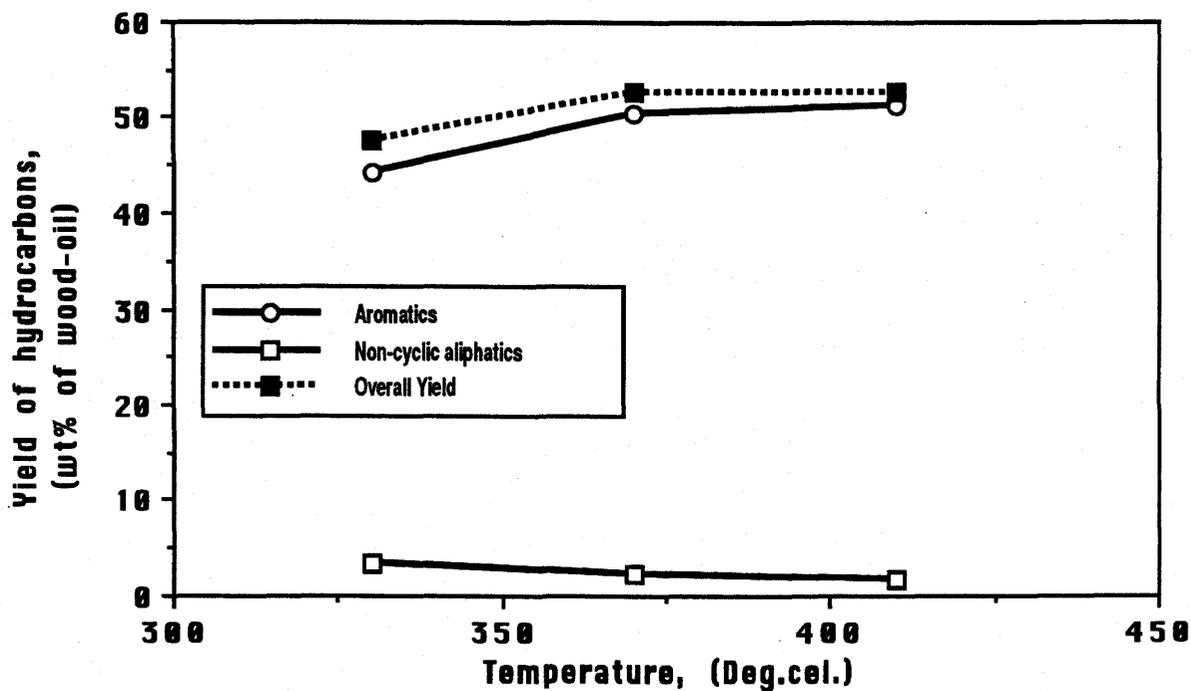


Figure 4.15 Effect of temperature on the yield of hydrocarbons (Wood-oil volatiles).

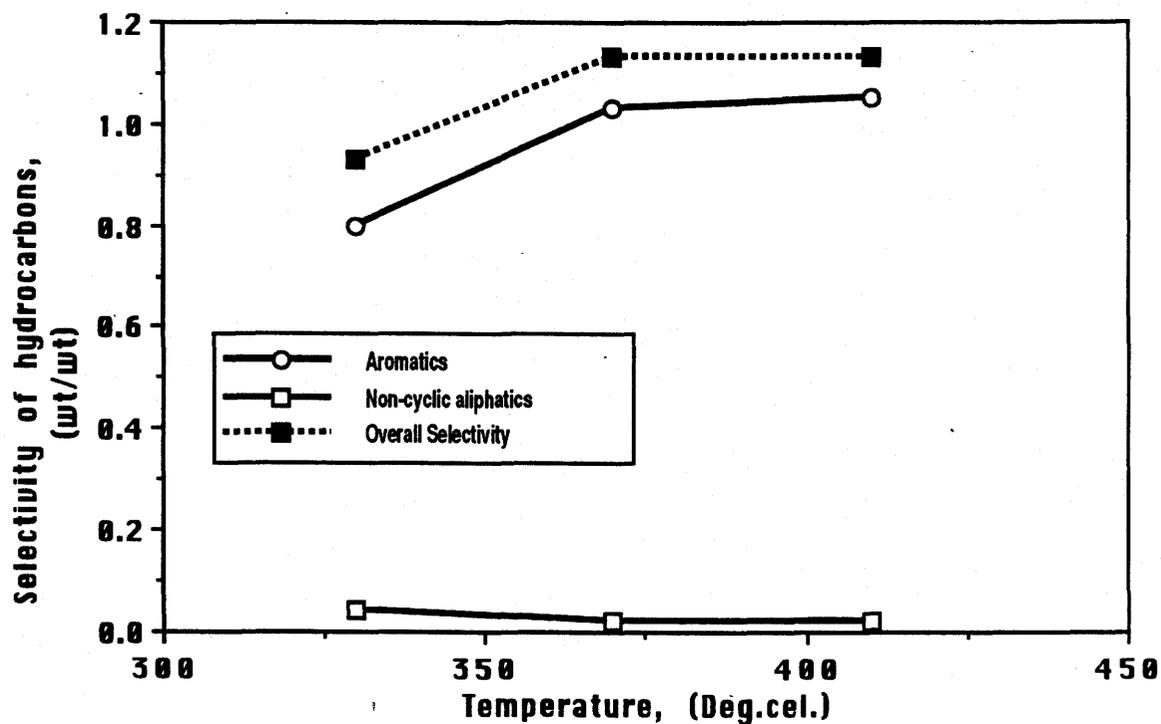


Figure 4.16 Effect of temperature on the selectivity for hydrocarbons (Wood-oil volatiles).

hydrocarbons (65 wt%) was obtained for the most volatile fraction, i.e. the fraction that vaporized up to 150 °C. This fraction represented only 21 wt% of the wood-oil compared to 64 wt% obtained in this work when separation was carried out at 200 °C and 172 Pa.

These results have shown that by separating the volatile fraction from the non-volatile fraction, higher organic distillate yields as well as higher hydrocarbon yields and selectivities could be obtained.

The reason for these improvements may be because the bulky non-volatile components of the wood-oil which are difficult to crack during processing were absent. These non-volatiles have molecular sizes that prevent easy access to the pores of the catalyst. On the other hand, they do polymerizes easily over the catalyst to form tar or coke. The tar or coke deposits or blocks the active sites and eventually results in catalyst deactivation. However, in the absence of these bulky molecules, the smaller volatile molecules find it easier to access the pores, react to form products and move out of pores with increased diffusion rates. Chantal et al. [1984] also noted that when the heavier components of wood-oil were present during processing, they led to tar formation. If the tars were allowed to stay in contact with the catalyst they significantly contributed to coke formation. Hence it is essential in the processing of wood-oils that a separation of the heavier fractions be implemented before catalytic

conversion.

It has been shown in this work that the wood-oil or its volatile fraction could be upgraded over HZSM-5 catalyst to organic liquid products which are rich in gasoline range hydrocarbons. The gasoline products were entirely alkylated benzenes. This product would be expected to have octane ratings in excess of 100 [Diebold and Scahill, 1988] and could alternatively be blended with gasoline products of lower octane ratings. Due to the expected high demand for unleaded gasoline with high octane numbers, the gasoline made by this process would be expected to command competitive prices if sold to the petroleum refinery industries for blending purposes.

Also, by separation from the parent organic distillate, the aromatic and phenolic fractions could be used as a source of useful chemicals. The benzene could be used as a chemical intermediate. Benzene has a widespread application in chemical synthesis of styrene, phenol and cyclohexane production. The alkyl benzenes could be used in the production of detergents. Toluene finds very important use in hydrodealkylation processes, solvents, benzylchloride, benzoic acid and phenol production. Toluene also finds use in the production of caprolactam, a monomer for the production of nylon. Xylenes have developed extensively as a chemical raw material. The first isomer to achieve commercial significance was o-xylene which has been used for phthalic anhydride manufacture.

However, in this work o-xylene yields were relatively small compared to p-xylene. The p-xylene can be used in the manufacture of terephthalic acid which is an essential compound needed for fibre production [Waddams, 1980]. Also, the phenolic fraction could be reacted with methanol to form methyl aryl ethers which are proven octane enhancers [Diebold and Scahill, 1988].

4.3. Phase 4: CONVERSION AND PERFORMANCE OF VARIOUS CATALYSTS IN UPGRADING WOOD OIL

So far, upgrading of wood-oils has been carried out with either HZSM-5 or hydrotreating catalysts such as Co-Mo and Ni-Mo. No information is available in the literature on the treatment of wood-oil with other catalysts. Therefore, it was of interest to investigate the effect of upgrading wood-oil with a variety of catalysts. The catalysts used in addition to HZSM-5 were silicalite, H-mordenite, H-Y and silica-alumina. The performance of each catalyst and the effect of catalyst acidity, pore size and crystallinity (shape selectivity) were studied.

4.3.1 Overall Product Distribution

The studies were carried out at 3.6 WHSV, 330 to 410 °C and atmospheric pressure. The products from upgrading over these catalysts included an aqueous fraction, coke, gas, residue, and organic liquid product (i.e., organic distillate). The mass balances at each temperature are presented in Table 4.11. In the following, the effect of temperature and catalyst type on the yield of each product are discussed.

4.3.1.1 Organic Distillate and Hydrocarbon Yields and Selectivity

As can be seen from Table 4.9 and 4.11, this fraction was between 53-63 wt%, 46-57 wt%, 55-63.5 wt%, 51-58 wt% and 40-67 wt% for silicalite, HZSM-5, H-mordenite, H-Y and silica-alumina, respectively. Since it was the objective of this work not only to produce high quantities of this fraction but also high quality, i.e., low oxygen and high hydrocarbon contents, the detailed analysis of the organic distillate and the yield and selectivity for hydrocarbons were evaluated for each catalyst.

Table 4.12 shows the composition of the organic distillate obtained for each catalyst after upgrading. As can be seen it was made up of aliphatic and aromatic hydrocarbons and oxygenated compounds with composition varying with reaction temperature. The oxygenated compounds consisted of various ketones, phenols, alcohols and furans. The detailed composition has been presented in Appendix D.7.

Effect of Temperature on Hydrocarbon Formation

The yields of hydrocarbons with temperature for each catalyst is shown in Figure 4.17. With the exception of HZSM-5 which had a maximum yield at 370 °C, the yields of hydrocarbons from the other catalysts increased progressively with temperature. The decline at 370 °C in the hydrocarbon yield when using HZSM-5 may be the result of increased coke

Table 4.12

Effect of temperature and catalyst type on the composition of organic distillate.

| Catalyst | Silicalite | | | Mordenite | | |
|-----------------------------------|------------|-------|-------|----------------|-------|-------|
| | 330 | 370 | 410 | 330 | 370 | 410 |
| Temperature, °C | | | | | | |
| Composition | | | | | | |
| Aliphatic Hydrocarbons | 2.0 | 3.3 | 2.9 | 11.1 | 10.1 | 12.3 |
| Aromatic Hydrocarbons | 15.0 | 23.1 | 31.9 | 19.5 | 23.1 | 33.9 |
| ¹ Oxygenated Compounds | 58.7 | 58.0 | 47.9 | 53.0 | 50.9 | 38.4 |
| Unidentified | 16.4 | 15.9 | 15.4 | 14.3 | 15.6 | 17.3 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Catalyst | HY | | | Silica-alumina | | |
| | 330 | 370 | 410 | 330 | 370 | 410 |
| Temperature, °C | | | | | | |
| Composition | | | | | | |
| Aliphatic Hydrocarbons | 7.6 | 9.1 | 11.2 | 15.3 | 13.5 | 20.4 |
| Aromatic Hydrocarbons | 22.7 | 24.4 | 27.9 | 5.7 | 6.3 | 18.7 |
| ¹ Oxygenated Compounds | 52.5 | 50.0 | 34.4 | 58.9 | 51.3 | 42.2 |
| Unidentified | 20.1 | 18.9 | 18.7 | 17.2 | 16.5 | 16.2 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Catalyst | HZSM-5 | | | | | |
| | 330 | 370 | 410 | | | |
| Temperature, °C | | | | | | |
| Composition | | | | | | |
| Aliphatic Hydrocarbons | 3.2 | 4.0 | 2.7 | | | |
| Aromatic Hydrocarbons | 62.7 | 66.7 | 60.9 | | | |
| ¹ Oxygenated Compounds | 23.0 | 19.4 | 20.1 | | | |
| Unidentified | 11.1 | 9.9 | 16.4 | | | |
| Total | 100.0 | 100.0 | 100.0 | | | |

¹ Includes mainly ketones, phenols, alcohols and furans.

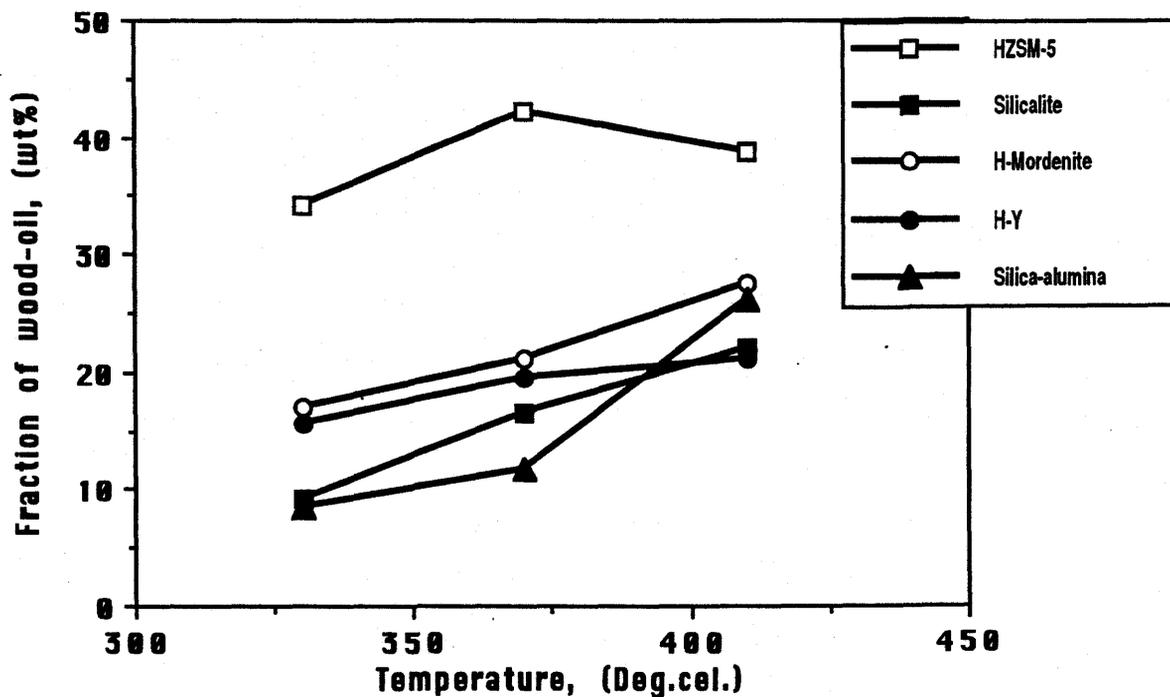


Figure 4.17 Yield of hydrocarbons with temperature and catalyst type.

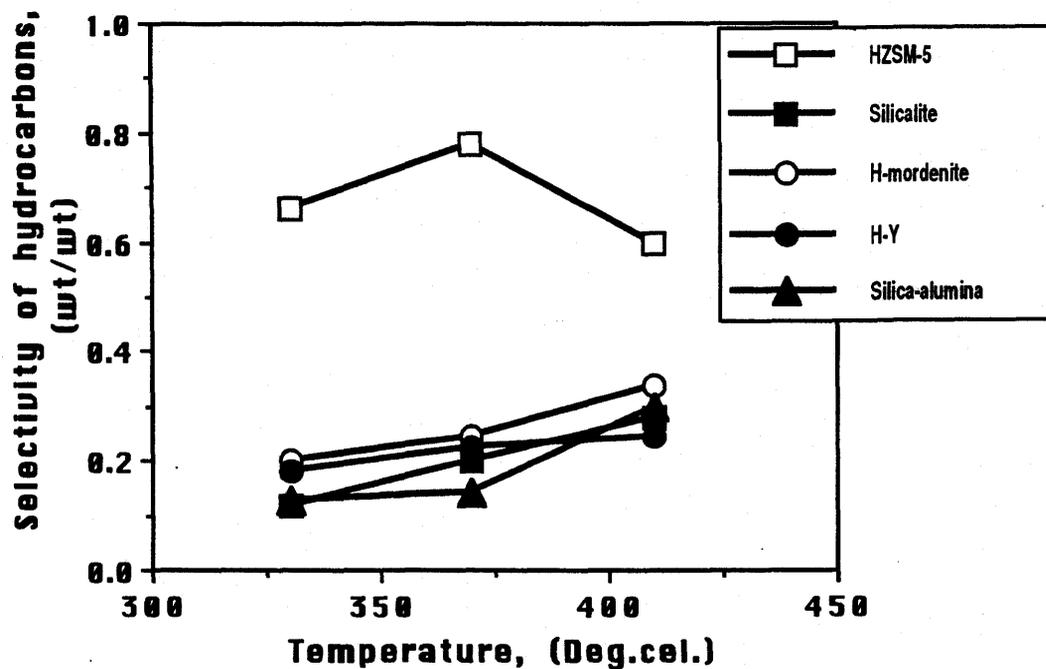


Figure 4.18 Effect of temperature and catalyst type on overall hydrocarbon selectivity.

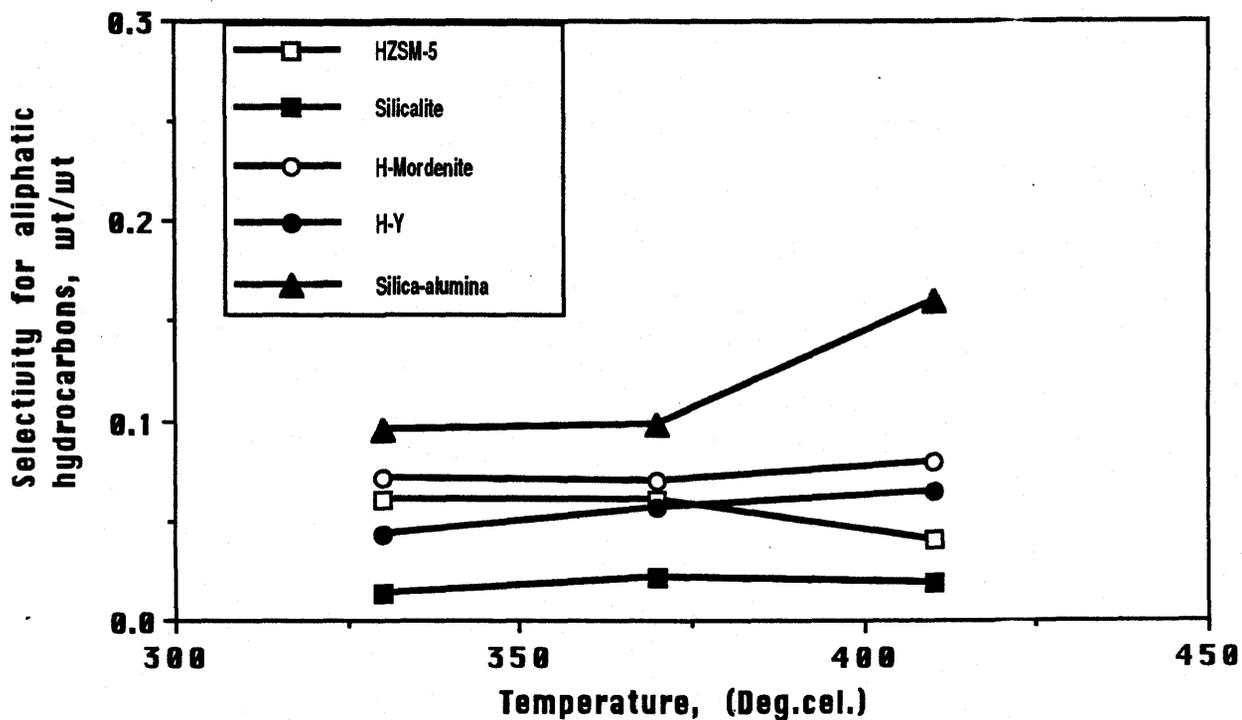


Figure 4.19a Effect of temperature and catalyst type on selectivity for aliphatic hydrocarbons.

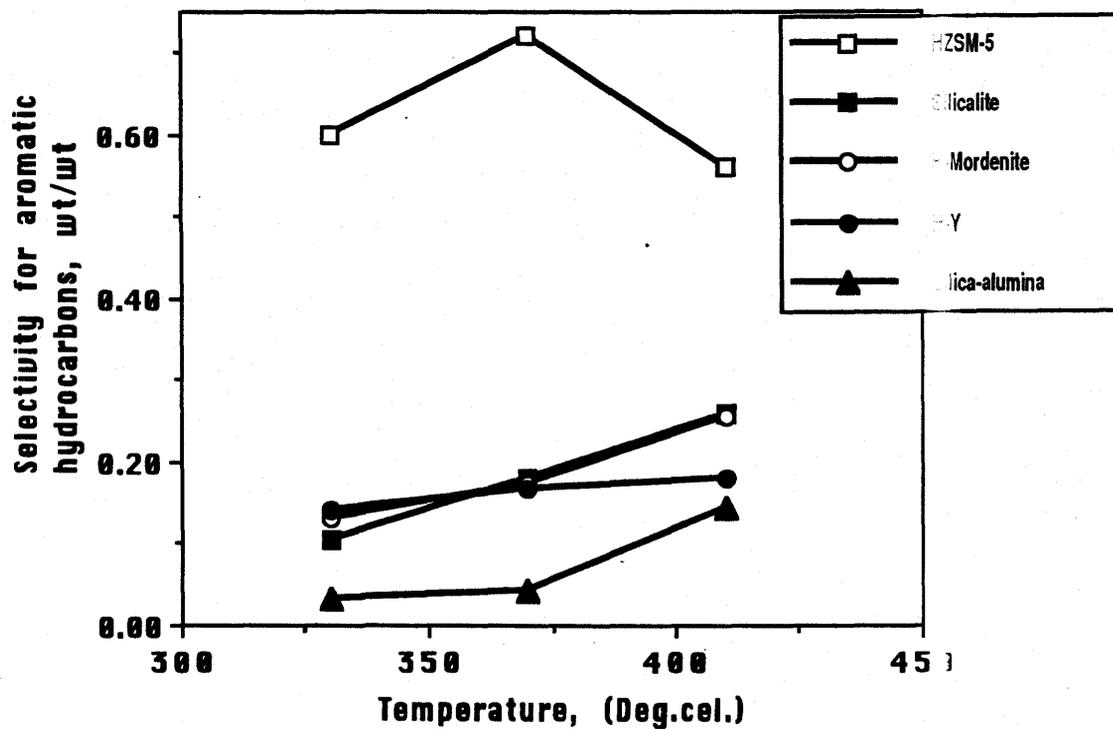


Figure 4.19b Effect of temperature and catalyst type on selectivity for aromatic hydrocarbons.

forming reactions involving the aromatic portion of the hydrocarbons. It has been reported [Wojciechowski and Corma, 1986; Chen et al., 1989] and generally accepted that aromatic compounds are intermediates or precursors for the formation of coke. Figures 4.18 and 4.19a and b show the selectivities for total hydrocarbons, aliphatic and aromatic hydrocarbons, respectively. Again, the selectivity was affected by reaction temperature since diffusion and reaction rates are temperature dependent. With the exception of silica-alumina, the selectivity for aromatic hydrocarbons was significantly higher than aliphatic hydrocarbons. This observation may be explained in terms of the enhanced aromatization reactions induced by the folding effect of the shape selective zeolites [Weisz et al., 1979].

Appendix D.7 shows the yield of the major hydrocarbon compounds identified in the organic distillate fraction. For the medium pore zeolites, i.e., HZSM-5 and silicalite, benzene, toluene, xylene and alkylated benzenes were the major compounds. On the other hand, the large pore zeolites contained alkylated benzenes in addition to polycyclic aromatic hydrocarbons such as indene based compounds (Appendix D.9c and d). The major compounds were C₉ to C₁₃ hydrocarbons. Unlike the shape selective catalysts, amorphous silica-alumina produced higher fractions of aliphatic than aromatic hydrocarbons with no defined distribution. The yields of these compounds mostly increased with reaction temperature.

4.3.1.2 Yields of Other Products

Aqueous Fraction

The production of aqueous fractions during upgrading indicates that dehydration was one way by which deoxygenation occurred with the oil. Since deoxygenation was a major concern of upgrading, it was essential to measure how much dehydration took place on each catalyst. This would aid in selecting the best deoxygenating catalyst. As can be seen HZSM-5 was the most outstanding dehydration catalyst. Recalling from section 4.1 that the wood-oil consisted of various acids, alcohols, furans, ketones, aldehydes, HZSM-5 has been reported [Chang and Silvestri, 1977; Chen et al., 1989] to effectively dehydrate most of these compounds through carbenium ion mechanisms to produce water.

The reason why HZSM-5 compared to the other catalysts was a better dehydrating catalyst may be explained from the standpoint of pore size, diffusion and reaction. The volatile fraction of the wood-oil which makes up about 60 wt% can be effectively reacted in medium pore than large pore zeolites. This is because the kinetic diameter of most of the volatile molecules are far lower than the pore size of the large pore zeolites and can flow through without reacting. However, with HZSM-5 these can enter and a larger fraction can react on the active sites in HZSM-5.

Also, comparing acidic and non-acidic zeolites, i.e., HZSM-5 and silicalite, it can be seen that dehydration was

enhanced with the inclusion of catalytically acid sites.

Coke Formation

In general coke formation increased monotonically with reaction temperature for all catalysts implying that coke was one of the final products of the conversion process. Coke formation has been reported [Chantal et al., 1984, Guisnet et al., 1986] to take place on both the inner pores and surface of zeolites. Comparing large and medium pore zeolites, it can be seen that coke formation was higher with larger pore zeolites than the medium pore zeolites. Guisnet et al. [1986] used the n-heptane cracking on H-Y and HZSM-5 to explain the differences in coke formation between medium and large pore zeolites. It was suggested that coke was initially formed in the supercages of large pore zeolites and channel intersections of medium pore zeolites. Due to steric hindrances near active sites, coke formation was usually slower on HZSM-5 than H-Y. This may explain the reason why coke formation was higher with large pore zeolites than medium pore zeolites. Also, it was observed that as a result of pore size constraints the coke formed consisted of mono and biaromatics on HZSM-5 and polyaromatics on H-Y.

Coke formation on silica-alumina was also relatively high and comparable in quantity with the large pore zeolites. But in this case the coke may have been formed through polymerization and/or condensation reactions on the surface of

the catalyst [Campbell, 1983].

Gas Formation

The gas produced from all the catalyst increased monotonically with temperature, again implying that gas was a final product of the conversion process. The composition of the gas was also an indication of cracking and deoxygenation effectiveness. The gas formed consisted mainly C₁ to C₅ hydrocarbon gases, carbon monoxide and dioxide. For the medium pore zeolites, C₃ and C₄ hydrocarbon gases were the main product gases, whereas for silica-alumina and the large pore zeolites, the hydrocarbon gases were distributed fairly evenly along C₁ to C₄ carbon numbers.

As mentioned previously, the production of carbon monoxide and dioxide was an indication that deoxygenation of the wood-oil also proceeded through decarboxylation reactions. The carbon oxides made up about 3.0-6.0 wt%, 3.0-5.5 wt%, 1.0-5.5 wt%, 2.0-4.6 wt%, and 4.0-9.0 wt% of the gas product for silicalite, H-mordenite, H-Y, silica-alumina and HZSM-5, respectively. This again shows HZSM-5 to be the better deoxygenating catalyst.

4.3.2 Performance of Catalysts

As shown above, the wood-oil was processed over the catalysts to various extents. In upgrading of wood-oils, maximizing the yield of hydrocarbons, achieving various

extents of deoxygenation, reduction in coke formation or conversion of non-volatile fraction [Chantal et al., 1984; Baker and Elliot, 1988, Chen et al., 1988, Sharma and Bakhshi, 1989, 1991a] are some of the major objectives. Since no information is available in the literature on the processing of wood-oils using these catalyst, it was essential to determine the relative performance of each catalyst in relation to some of these objectives (or performance criteria). It was also important to compare their performance with that of HZSM-5 catalyst which has been used extensively in wood-oil upgrading. Some of these aspects are discussed in the following.

4.3.2.1 Yield of Hydrocarbons

Since the production of hydrocarbons is a major objective of most wood-oil upgrading work, the yield of hydrocarbons was selected as one of the measures of catalyst performance. Optimum yields of hydrocarbons for HZSM-5 catalyst were at 390 °C and for the other catalyst, at 410 °C. These were 42.1 wt% for HZSM-5, 22.1 wt% for silicalite, 27.5 wt% for H-mordenite, 21.0 wt% for H-Y and 26.2 wt% for silica-alumina catalyst. The yield with temperature is plotted in Figure 4.17 and follows the order: HZSM-5 > H-mordenite > H-Y > silicalite, silica-alumina. This shows that HZSM-5 was the best catalyst in the conversion to hydrocarbons.

4.3.2.2 Selectivity for Hydrocarbons

The hydrocarbon selectivity was also used as a measure of catalyst performance since hydrocarbon formation was a major objective. The importance of calculating the selectivity for hydrocarbons has already been mentioned in section 4.3. The selectivities were calculated by equation 4.1 for aromatic, aliphatic hydrocarbons and the overall hydrocarbon selectivity. These are plotted in Figures 4.18 (overall hydrocarbons), 4.19a (aliphatics) and 4.19b (aromatics). It can be seen from Figure 4.19a that the selectivity for aliphatic hydrocarbons was highest for silica-alumina catalyst and followed the general order: silica-alumina > H-mordenite > HZSM-5, H-Y > silicalite. On the other hand, the selectivity for aromatic hydrocarbons was highest for HZSM-5 and followed the general order: HZSM-5 > H-mordenite, silicalite, H-Y > silica-alumina.

The most significant observation from these results was the relatively high aliphatic selectivity and low aromatic selectivity that were obtained when silica-alumina was used. This may be because of the absence of shape selectivity properties. The presence of defined pore sizes which typifies zeolites have been mentioned [Weisz, 1979; Dyer, 1986; Chen et al., 1989] to enhance the selectivities for aromatic hydrocarbons. The overall hydrocarbon selectivity as shown in Figure 4.18 followed the order: HZSM-5 > silicalite, H-mordenite > H-Y > silica-alumina. This shows that HZSM-5 has the

best selectivity for hydrocarbons.

4.3.2.3 Extent of Deoxygenation

Processing of wood-oils differs from processing of petroleum or coal liquids because of the importance of deoxygenation [Baker and Elliot, 1988]. Wood-oils contain between 20 to 40 wt% oxygen content so that one aim of most upgrading work has been to reduce this fraction to much lower values. Due to the high oxygen content, direct use often results in low heating values. Also, where motor fuels are desired, it is required that the oxygen content be reduced to levels between 100 and 1000 ppm [Kaliaguine, 1981]. As a result, it was essential to measure the performance of each catalyst in terms of its ability to deoxygenate the wood-oil. As mentioned earlier, deoxygenation during wood-oil upgrading was achieved through dual processes of dehydration and formation of carbon oxides.

Table 4.13 presents the elemental analyses of the feed and organic distillate obtained at 370 and 410 °C for each catalyst. As can be seen, the oxygen content was reduced from 15.2 wt% in the feed to minimum 4.1 wt% for silicalite, 5.1 wt% for H-mordenite, 4.0 wt% for H-Y, 3.4 wt% for Silica-alumina and 1.5 wt% for HZSM-5. The extent of deoxygenation (% deoxygenation) for each catalyst at 370 and 410 °C are also shown in Figure 4.20. From this Figure, deoxygenation was highest when using HZSM-5 and decreased in the order of

Table 4.13
Elemental analyses of feed (wood-oil + tetralin) and organic distillate obtained after upgrading using various catalysts.

| | Feed | Silicalite | | H-Mordenite | |
|---------------------------|-------------|-------------------|-------------|-----------------------|-------------|
| Temperature, °C | | 370 | 410 | 370 | 410 |
| Element | | | | | |
| Carbon | 75.4 | 86.7 | 85.7 | 84.7 | 85.8 |
| Hydrogen | 9.4 | 9.2 | 9.0 | 9.1 | 9.1 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| ¹Oxygen | 15.2 | 4.1 | 5.3 | 6.2 | 5.1 |
| % Deoxygenation | | 73.0 | 65.3 | 59.1 | 66.6 |
| | | HY | | Silica-alumina | |
| Temperature, °C | | 370 | 410 | 370 | 410 |
| Element | | | | | |
| Carbon | 87.2 | 86.8 | 87.9 | 87.6 | |
| Hydrogen | 8.8 | 8.7 | 8.0 | 9.0 | |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 | |
| ¹Oxygen | 4.0 | 4.5 | 4.1 | 3.4 | |
| % Deoxygenation | 73.3 | 70.8 | 73.3 | 77.8 | |
| | | HZSM-5 | | | |
| Temperature, °C | | 370 | 410 | | |
| Element | | | | | |
| Carbon | 88.9 | 89.2 | | | |
| Hydrogen | 9.6 | 9.1 | | | |
| Nitrogen | 0.0 | 0.0 | | | |
| ¹Oxygen | 1.5 | 1.7 | | | |
| % Deoxygenation | 90.1 | 88.8 | | | |

¹ Determined by difference.

silica-alumina, HY, silicalite and H-mordenite. Comparing silicalite and HZSM-5, it can also be mentioned that the possibility of acid-catalyzed deoxygenation reactions provided better deoxygenation when using HZSM-5 than Silicalite [Chang, 1983; Chen et al., 1989]. This is because silicalite possesses essentially no acid sites [Flanigen et al., 1978]. On the other hand, the process of deoxygenation by the other catalyst is not understood.

4. Conversion of Non-volatile Fraction

As mentioned previously, one of the major objectives of most upgrading work has been to completely crack the 40 to 45 wt% high molecular weight or non-volatile fraction of the wood-oil to fractions that are relatively volatile [Sharma and Bakhshi, 1989]. Catalysts are therefore selected to meet this objective. In this section, the performance of the catalysts are determined by their ability to converted the non-volatile fraction by measuring the fraction of non-volatile residue in the product stream. The lower this fraction the better the catalyst performance.

The results are shown in Figure 4.21. As can be seen, the residue fraction decreased with increase in temperature for each catalyst. The results also show that the larger the pore size, the lower the conversion of non-volatile fraction. For instance, at 370 °C the non-volatile residue for HZSM-5, (5.4 Å), H-mordenite (6.4 Å) and H-Y (8.4 Å) were 21.5, 22.1 and

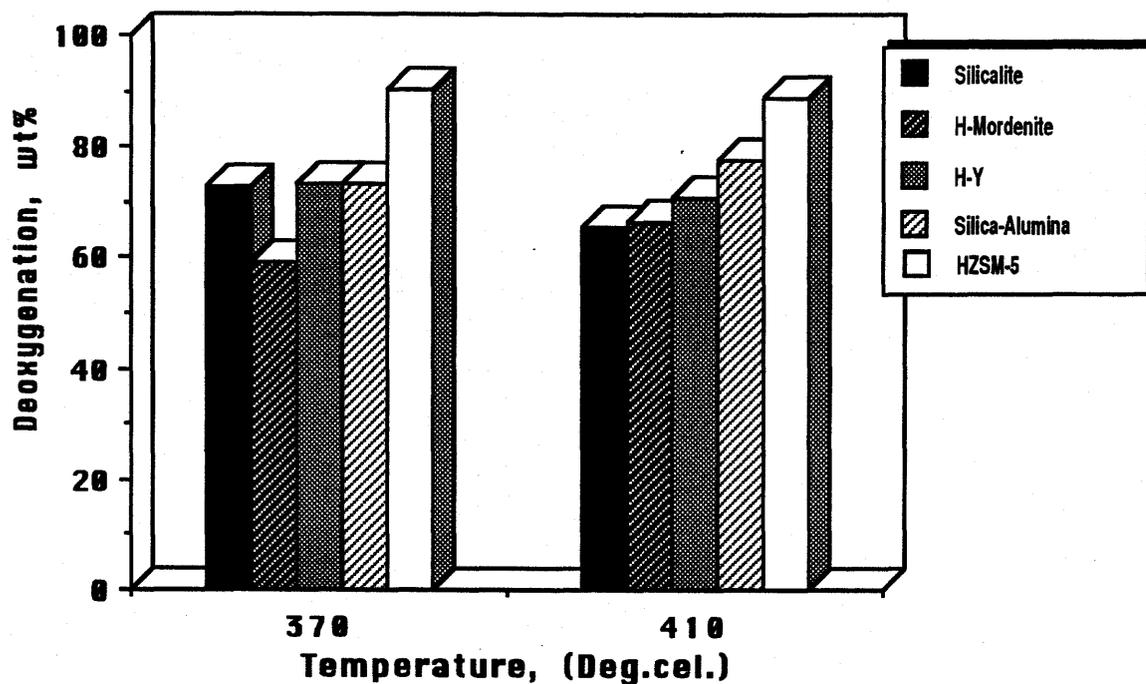


Figure 4.20 Extent of deoxygenation of wood-oil by catalysts at different temperatures.

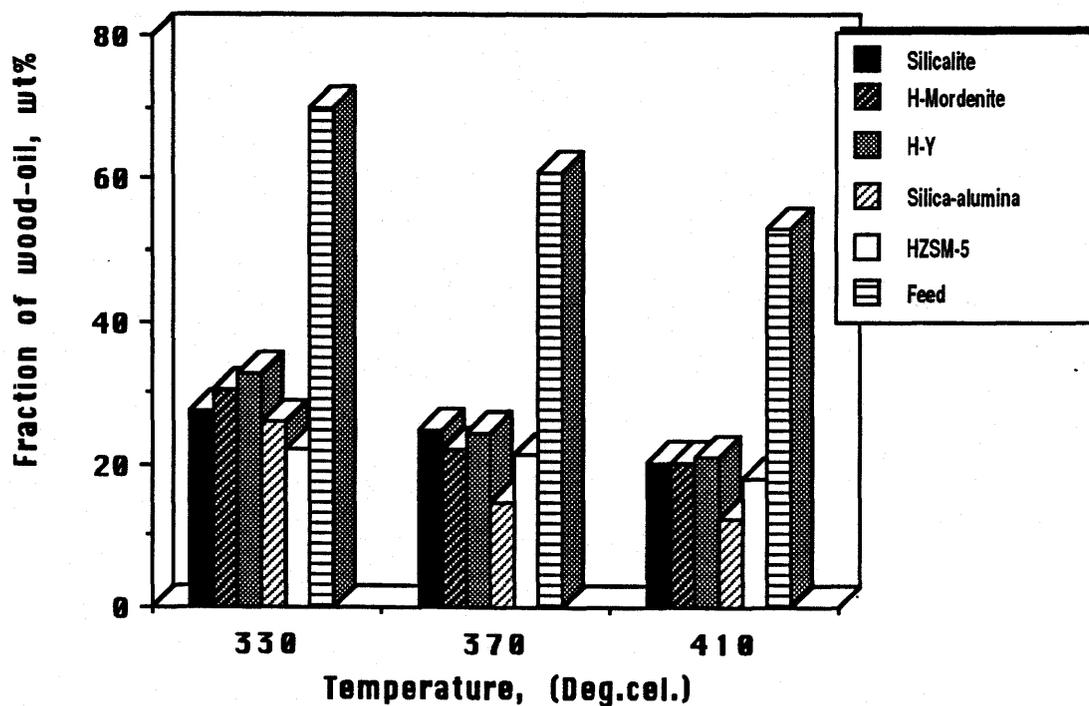


Figure 4.21 Fraction of non-volatile residue remaining after catalytic treatment.

24.6 wt%, respectively. Also, comparing acidic HZSM-5 (17.9 to 22.3 wt%) and non-acidic silicalite (20.1 to 27.5 wt%), it can be seen that catalyst acidity may have played a major role in the cracking of the non-volatile fraction. It has been mentioned that protons are involved in carbenium ion intermediates which are species responsible for acid-catalyzed cracking [Pines, 1981; Chen et al., 1989]. It can also be seen that the non-zeolite silica-alumina catalyst was more effective in the conversion of the non-volatile fraction than the zeolite catalysts. On the contrary, it has been mentioned [Campbell, 1983] that acidic zeolite catalysts are about four orders of magnitude more active than non-zeolite silica-alumina catalysts in their performance as cracking catalysts. This has been attributed to the inclusion of Bronsted acid sites.

This study has shown that the conversion of the non-volatile fraction may be a combination of catalyst acidity, temperature effects and pore size. The overall performance followed the general order: silica-alumina > HZSM-5 > silicalite, H-mordenite > H-Y. It has also been shown that the large pore zeolites are the worst performers in cracking of non-volatiles.

5. Coke Formation

As mentioned earlier, coke formation is one of the most insidious problems of wood-oil processing since it results in

deactivation of the catalyst. In most catalytic processes it is unavoidable. However, by proper selection of catalysts or process conditions, coke formation can be minimized [Chantal, 1984; Chen, et al., 1988]. In the light of this, it was essential to measure the catalyst performance in terms of coke formation. The catalyst producing the least coke was considered the better catalyst.

Figure 4.22 shows plots of coke formation with temperature for each catalyst. It can be seen that generally, coke formation increased with pore size of the catalyst. The role of zeolite pore size on coke formation has already been mentioned in section 4.4.4. Also, it was lower with the non-acidic catalysts (silicalite) than acidic catalysts (HZSM-5). This may be because of the low extents of aromatic hydrocarbon formation when using silicalite since some of the hydrocarbons formed polymerized to coke. From these plots it can be seen that the performance was of the order: silicalite > HZSM-5 > H-mordenite > silica-alumina > H-Y.

4.3.3 Effect of Catalyst Pore Size/Structure on Hydrocarbon Formation

The nature and size of hydrocarbon molecules formed can be seen to be a direct function of the pore size and structure of the catalyst. A study of the hydrocarbon distribution by carbon number from the zeolite catalysts shown in Figure 4.23

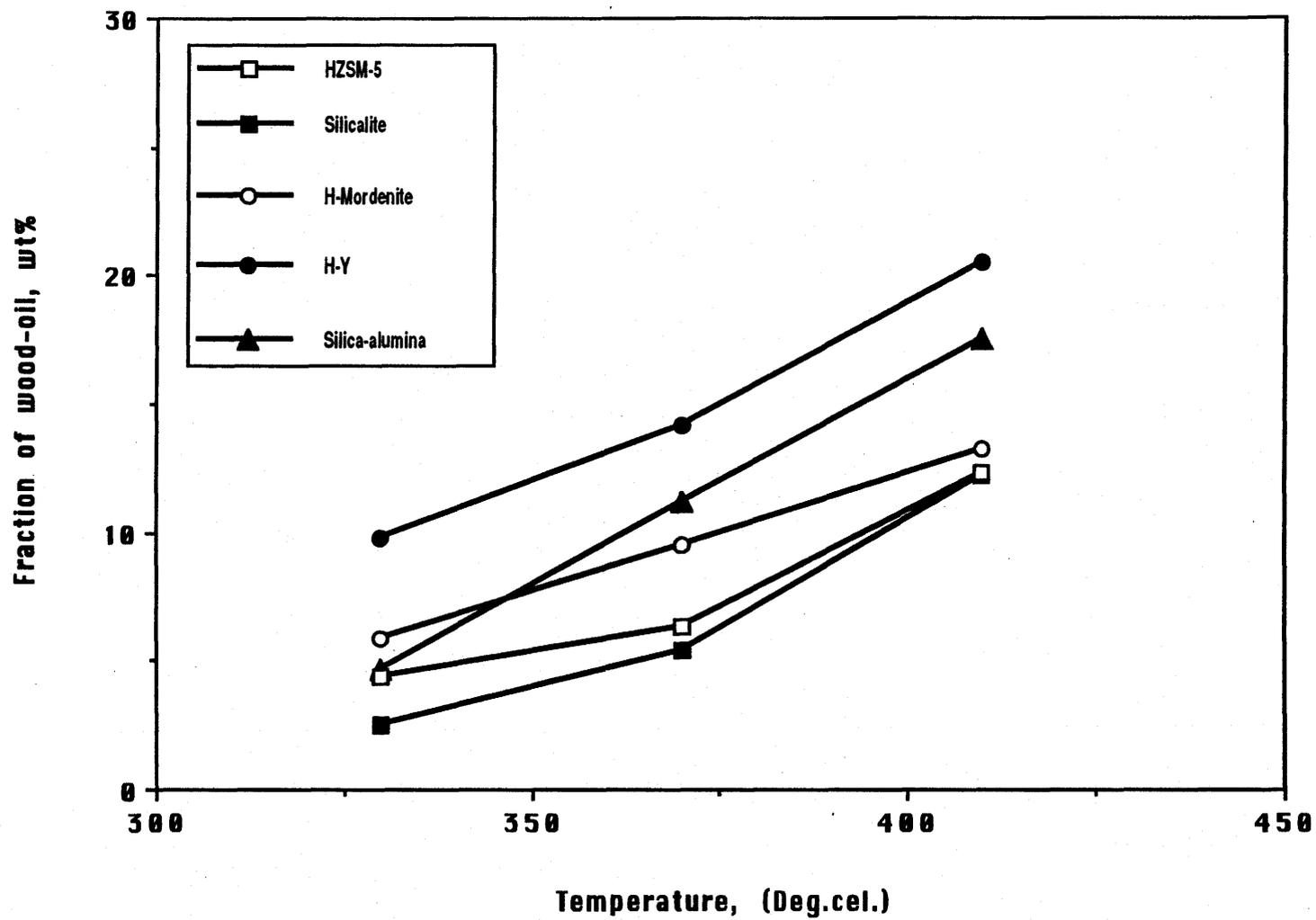


Figure 4.22 Coke formation from catalysts at different temperatures.

to 4.27 appears to confirm this. The products from medium pore zeolites mainly fall within the gasoline boiling point range (C_6 to C_{12}), and that for the large pore zeolites within the kerosene boiling range (C_9 to C_{15}). The selectivities were highest for C_6 to C_8 (medium pore) and C_9 to C_{12} (large pore zeolites) hydrocarbons, respectively. The pore size in addition to its structure has been mentioned to induces the selectivity nature of zeolite catalysts [Guisnet et al., 1986; Soltes et al., 1987; Szostak, 1989]. These properties determine the maximum size of molecules that diffuse into the pores, the maximum size to which small molecules can grow, long molecules crack or "folded", and products diffuse out into the product stream. This has been described by reactant, transition state and product selectivity properties of zeolites [Chang, 1983, Dyer, 1988].

4.3.4 Effect of Three-dimensional Framework (shape selectivity) on Hydrocarbon Formation

The role of shape selectivity characteristics on wood-oil upgrading can be understood by comparing the crystalline aluminosilicates zeolites to amorphous mixed-oxide silica-alumina in terms of distribution of hydrocarbons by carbon number. As mentioned earlier, zeolites have a well defined pore size and structure that determines which molecules should enter its pores, which intermediates should form and which products should diffuse into the product stream, i.e. shape

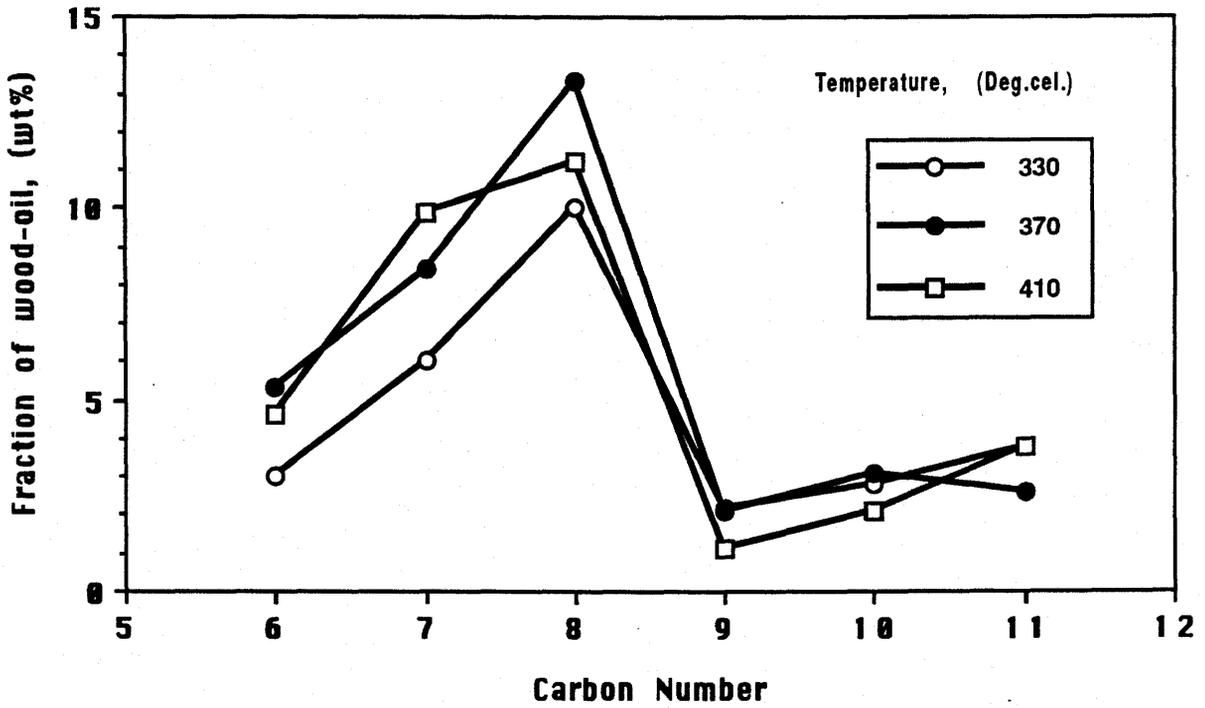


Figure 4.23 Distribution of hydrocarbons by carbon number when using HZSM-5.

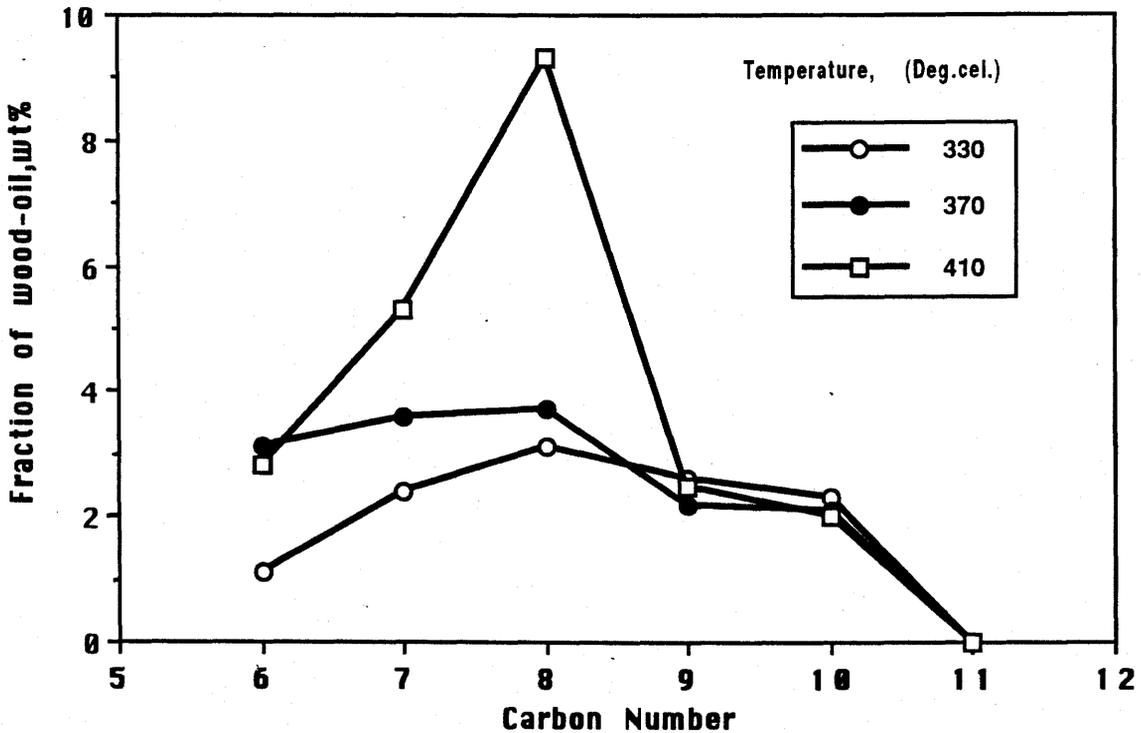


Figure 4.24 Distribution of hydrocarbons by carbon number when using silicalite.

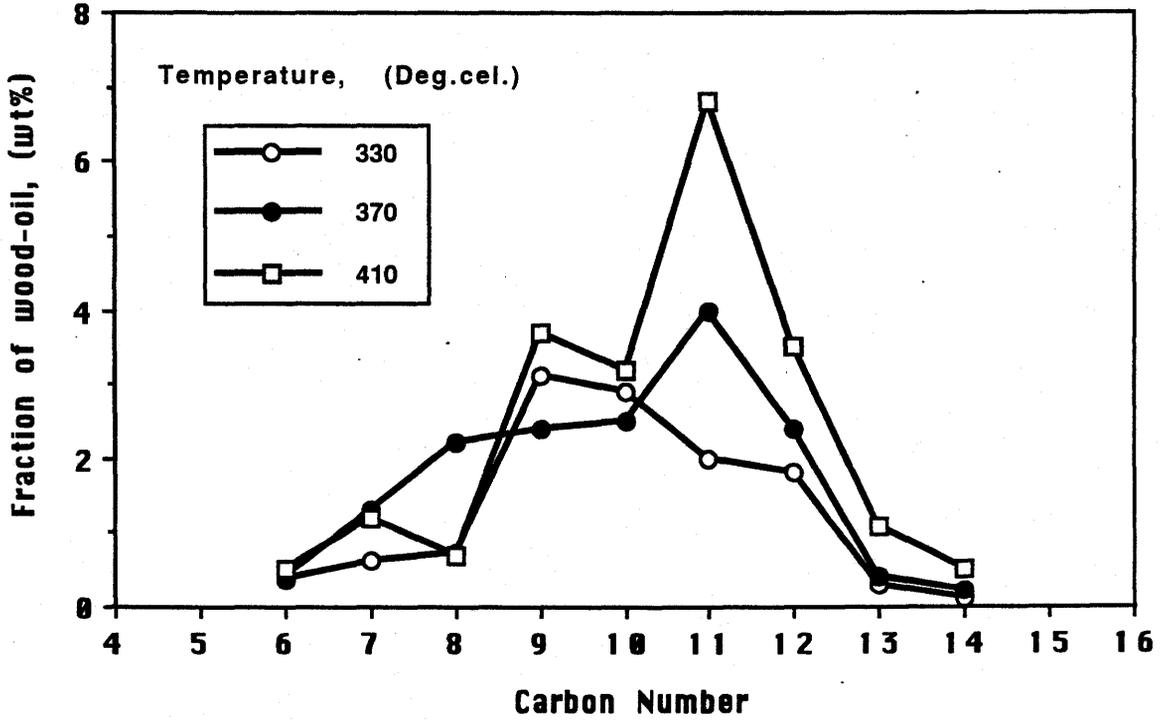


Figure 4.25 Distribution of hydrocarbons by carbon number when using H-mordenite.

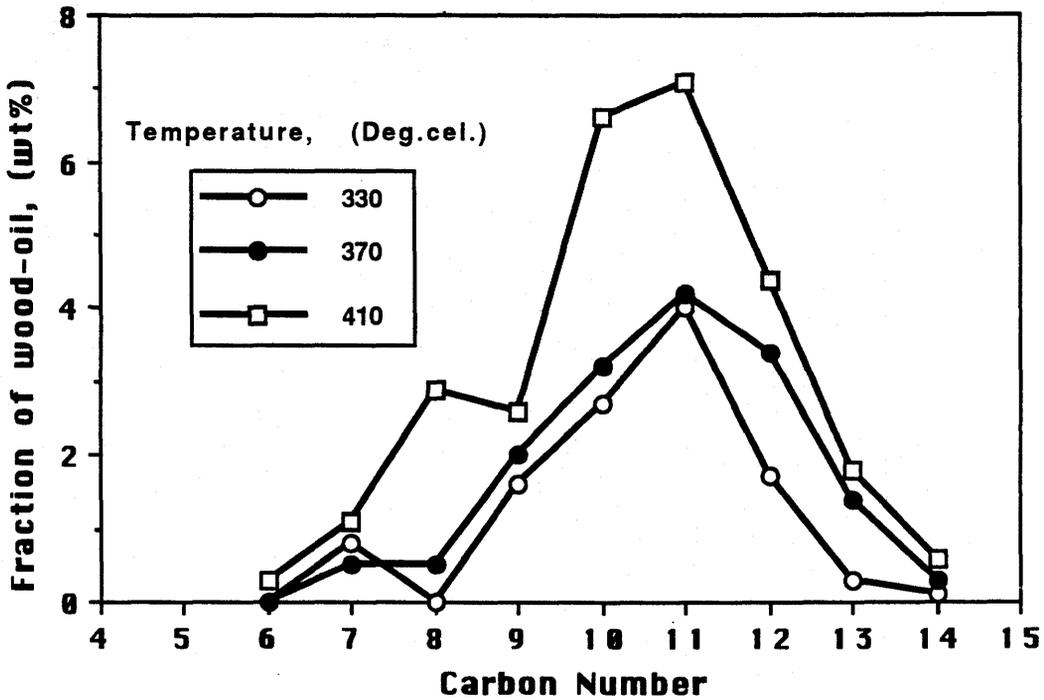


Figure 4.26 Distribution of hydrocarbons by carbon number when using H-Y.

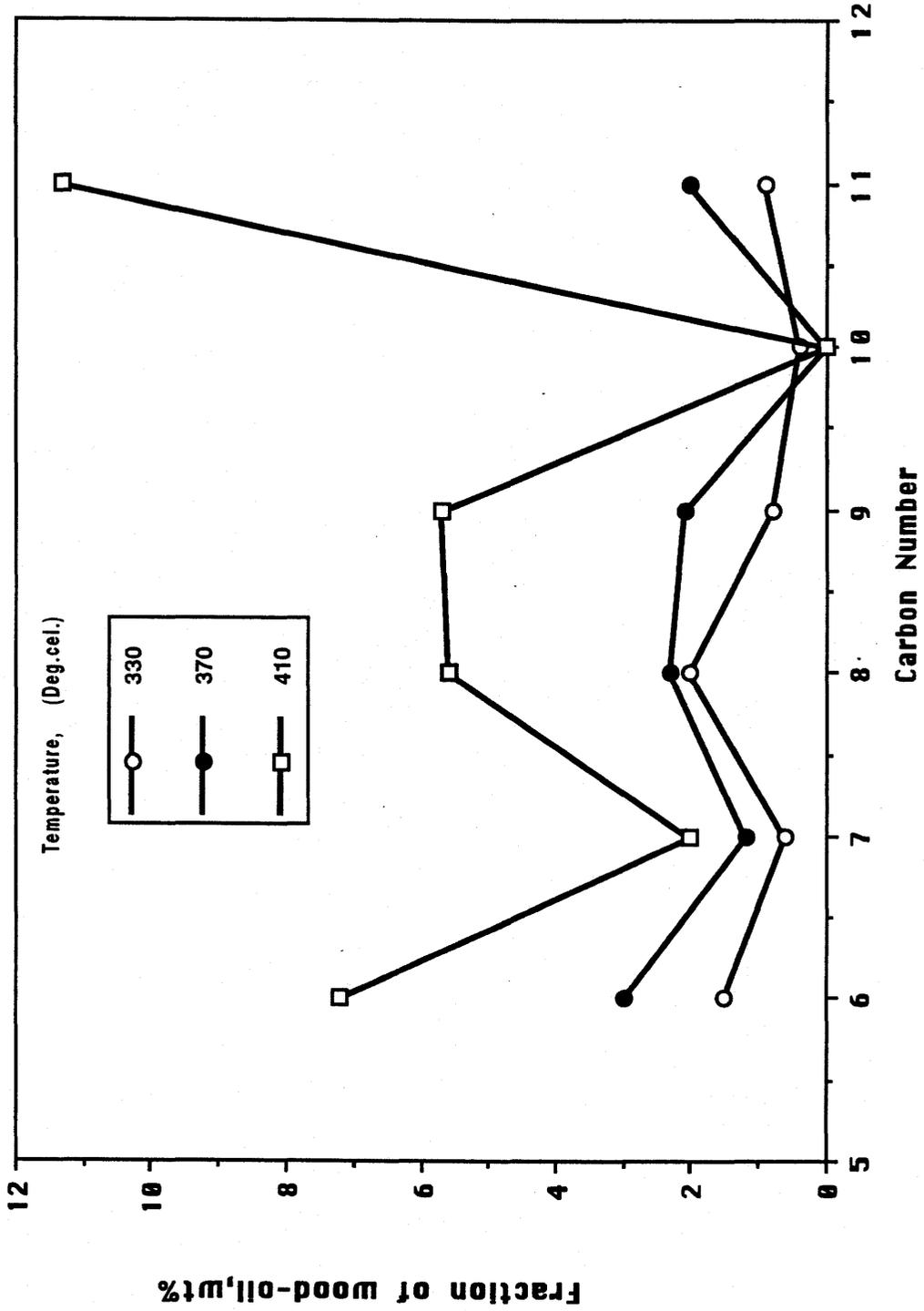


Figure 4.27 Distribution of hydrocarbons by carbon number when using silica-alumina.

selectivity characteristics. In effect, this determines the diffusion and reaction rates of molecules. As a result, the products of upgrading also show defined distributions (Figure 4.23 to 4.26). The advantage of this is that a particular zeolite can be used to obtain a desired product, with desired boiling points and distribution as in fuel processing [Probstein and Hicks, 1982]. For instance, zeolite H-Y could be used in processes where kerosene range hydrocarbons were desired. On the other hand, silica-alumina is amorphous and although it has both dehydrating and acid properties, reactions are primarily a surface phenomena. There are no size constraints (Figure 4.27), especially configurational diffusion constraints. Molecules can crack to individual units and others grow into larger units without any constraint from the catalyst. Temperature rather than pore size may be the determining factor in the yield of hydrocarbons for amorphous silica-alumina.

Also, the effect of zeolite shape selectivity can be studied by comparing the selectivity for aromatics and aliphatic hydrocarbons between the zeolite catalysts and non-zeolite silica-alumina. As shown in Figure 4.19a and b, when using the zeolite catalysts, the selectivity for aromatic hydrocarbons was significantly higher than for aliphatic hydrocarbons. On the other hand, when using a silica-alumina catalyst, the selectivity for aliphatic hydrocarbons was higher than that for aromatic hydrocarbons. This has been

explained by the tendency to cause molecules to be restructured in the pores of zeolite catalysts which has been mentioned [Weisz et al., 1979] to enhance aromatization reactions.

4.3.5 Effect of Catalyst Acidity on Hydrocarbon Formation

The role of acid sites on hydrocarbon formation can be well understood by comparing the yields of hydrocarbons (Figure 4.17) and the extent of deoxygenation between HZSM-5 and silicalite (Figure 4.20). The primary difference between the two catalysts is acidity. HZSM-5 possesses both Bronsted and Lewis acid sites [Chang, 1983; Szostak, 1989] whereas silicalite, which is a polymorph of ZSM-5 [Flanigen et al., 1978], (i.e., it has the same pore size and similar structure as HZSM-5) has no acid sites. Silicalite is made up of only silica molecules [Flanigen et al., 1978]. Also, catalyst activity has been mentioned [Szostak, 1989] to be proportional to catalyst acidity. Since catalytic deoxygenation, cracking and subsequent hydrocarbon forming reactions increase with acid sites, it appears that the absence of acid sites on the silicalite catalyst was one of the causes of the lower hydrocarbon yields (Figure 4.17).

The effect of catalyst acidity can also be studied by examining the quality of the hydrocarbon fraction in terms of the oxygen content. As shown in Table 4.13, a higher quality hydrocarbon-rich fraction was obtained for HZSM-5 (1.5 and 1.7

wt% oxygen) than silicalite (4.3 and 5.3 wt% oxygen). Also, only trace amounts of water were obtained when silicalite was used compared to 2.8 to 3.6 wt% when using HZSM-5. Since wood-oil deoxygenation is an acid catalyzed reaction, it can be seen that the absence of acid sites on silicalite may have resulted in the lower dehydration and higher oxygen contents of hydrocarbon-rich fraction.

Cracking rates are also enhanced by the presence of acid sites [Wojciechowski and Corma, 1986; Chen et al., 1989]. In Table 4.11 the fraction of residue remaining after catalytic treatment are higher for silicalite than HZSM-5, again suggesting the important role of acid sites in the cracking of high molecular weight feeds.

4.3.6 Tetralin Reactivity Over the Catalysts

As mentioned in Chapter 3, the wood-oil was co-processed with tetralin, so that it was essential to account for the reaction products of tetralin. Analysis of the reaction products showed that tetralin may have reacted through two major reaction routes; dehydrogenation and cracking (or dissociation) [Probstein, 1982; Hornell et al., 1982; Bockrath, 1983]. Table 4.7 summarizes these results in terms of the conversion and extent of dehydrogenation (defined as the naphthalene to tetralin (N/T) ratio). Conversions were up to 7 % for silicalite, 1.9 % for H-mordenite, 2.2 % for H-Y, and 0.9 % for silica-alumina compared to 6.0 % for HZSM-5.

In the first reaction route, i.e., the dehydrogenation of tetralin, the major products were naphthalene and hydrogen. In processes where hydrogen-donor solvents have been used, the naphthalene to tetralin ratio has been used as a measure of hydrogen transfer [Hornell et al., 1982]. As can be seen, this ratio ranged between 0.001 to 0.009. On the other hand, the major products of tetralin cracking or dissociation were mainly benzene, toluene, xylenes and a few tri-methylated benzenes. Both conversion and dehydrogenation were lowest for the silica-alumina catalyst. It has been mentioned [Campbell, 1983] that zeolites have more effective acidity and produces more catalytic cracking activities for hydrocarbons, even up to four orders of magnitude greater than silica-alumina. Tetralin conversion was higher for the medium pore zeolites (silicalite and HZSM-5) than for the large pore zeolites (H-mordenite and H-Y). This is probably because the pore size of H-mordenite and H-Y are so large that the tetralin molecule can diffuse through the pores with very little contact with the catalytically active sites. However, with the medium pore zeolites, diffusion rates are slower inside the pores and molecules have enough time to react before diffusing out of the pores.

The reaction products of tetralin were taken into account in calculating yields of the products with the assumption of negligible synergistic effects.

In this work, it has been shown that the wood-oil could be upgraded over different catalysts to hydrocarbon-rich products of various concentrations. It has also been shown that the catalyst acidity, pore size and structure, and shape selectivity influenced the yield and selectivity and distribution of the hydrocarbon products. H-Y and H-mordenite could be used to produce hydrocarbons within the kerosene boiling point range. This could be used as a jet fuel. silicalite and HZSM-5 could be used to provide hydrocarbons within the gasoline boiling point range. This could be used as motor fuel.

Various measures of catalyst performance were also defined. HZSM-5 was the superior catalyst where high yield and selectivity for hydrocarbons and high extents of deoxygenation were desired. For lower coke formation, silicalite was the best catalyst. For conversion of non-volatile fractions, silica-alumina was the best catalyst.

4.4 Phase 5: KINETIC MODELING I: MODEL COMPOUND STUDIES AND REACTION PATHWAYS

The main objective of this part of the research was to use model compound reactions as an aid in identifying and understanding the chemical steps for the conversion of the wood-oil. This information was used in deriving reaction pathway(s). The compounds studied were selected on a quantity basis from the main chemical groups identified in the volatile fraction of the wood-oil, i.e., acids, esters, aldehydes and ketones, alcohols, ethers and phenols. In this section, the results obtained are presented and discussed. The schematic approach shown in Figure 4.28 was followed in this study.

4.4.1 Reactivity of Acids and Esters

Propanoic acid and the methyl ester of acetic acid were used as model compounds to study the reactivity of acids and esters, respectively, over HZSM-5 catalyst. The reactivity data are presented in Table 4.14 for propanoic acid and in Appendix D.8 (conversion versus temperature) for methyl ester acetic acid. Since the reactivity of organic acids and their ester derivatives are similar [Morrison and Boyd, 1966], they are treated together in this section. The conversion of propanoic acid increased with temperature increase and also increased as the concentration was decreased. For each concentration, almost complete conversion was obtained at 410 °C.

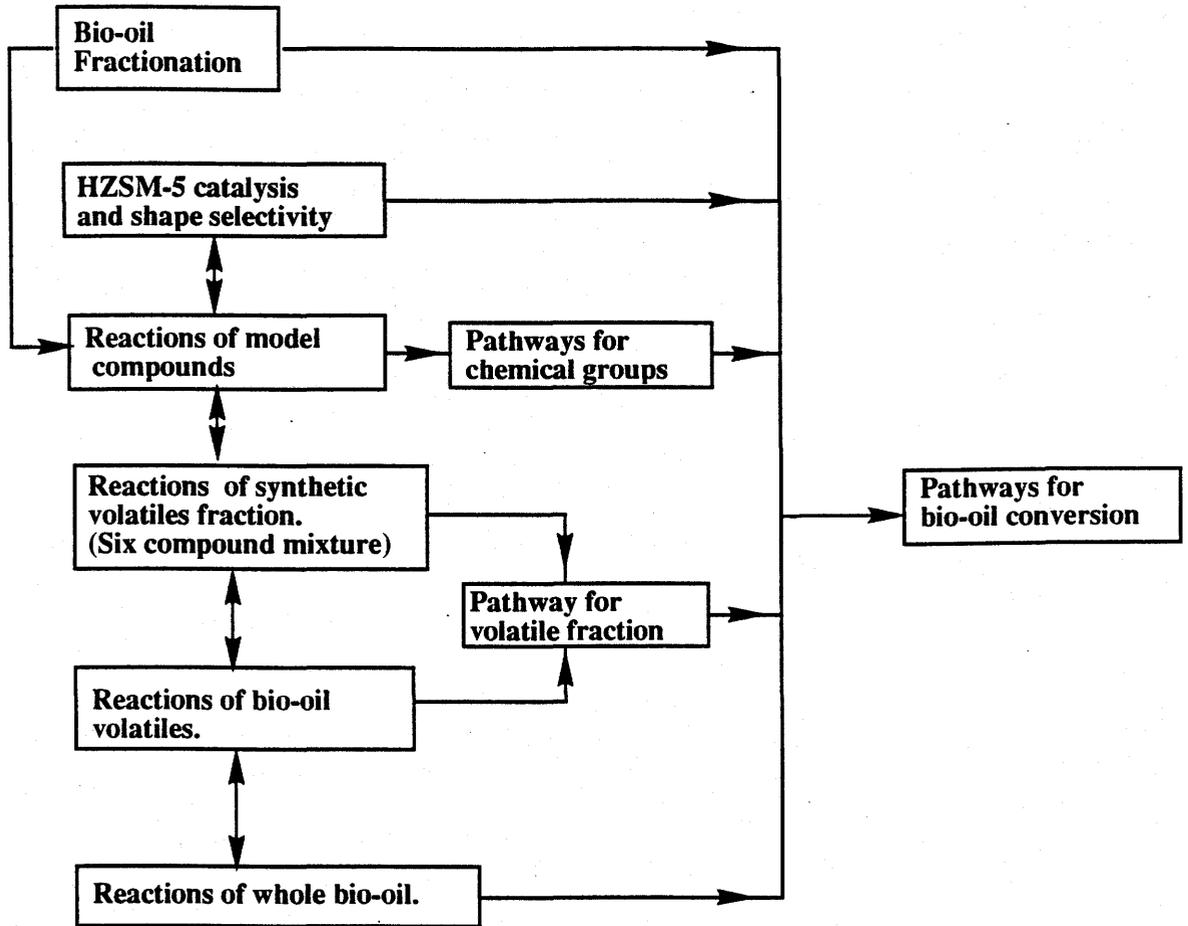


Figure 4.28 Schematic approach to reaction pathways for the conversion of wood-oil over HZSM-5 catalyst.

Table 4.14 continued.

Elemental analysis of Organic Distillate

| Element | Pure | 330 | 370 | 410 |
|------------------|------|------|------|------|
| Carbon | 39.9 | 38.7 | 86.9 | 87.8 |
| Hydrogen | 7.1 | 7.9 | 8.7 | 9.8 |
| Oxygen | 53.0 | 53.4 | 4.4 | 2.4 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 |
| Deoxygenation, % | | -1.0 | 91.7 | 95.5 |

Yield of major conversion compounds (wt% of organic distillate)

| CONCENTRATION, wt% | 100.0 | | | 18.35 | | |
|-----------------------------------|-------|-------|-------|-------|-------|-------|
| TEMPERATURE, °C | 330.0 | 370.0 | 410.0 | 330.0 | 370.0 | 410.0 |
| COMPOUNDS | | | | | | |
| Hexane | 0.0 | 2.4 | 4.4 | 6.3 | 10.6 | 5.4 |
| Formic acid, 1-methylpropyl ester | 0.0 | 0.0 | 0.6 | 1.0 | 1.5 | 0.0 |
| Pentane, 3-ethyl-2,2-dimethyl- | 0.0 | 0.0 | 0.1 | 5.0 | 3.5 | 0.0 |
| Benzene | 0.0 | 0.0 | 2.4 | 4.0 | 9.2 | 24.8 |
| Benzene, methyl- | 0.2 | 1.0 | 14.3 | 6.6 | 16.2 | 21.6 |
| Benzene, ethyl- | 0.0 | 0.2 | 2.5 | 2.9 | 4.2 | 5.7 |
| P-Xylene | 0.4 | 3.2 | 21.9 | 13.5 | 27.8 | 21.8 |
| o-Xylene | 0.0 | 0.0 | 2.1 | 1.4 | 3.1 | 4.4 |
| Benzene, 1,2,4-Trimethyl- | 0.0 | 1.0 | 3.5 | 3.6 | 5.6 | 1.8 |
| Benzene, methylethyl- | 0.0 | 0.0 | 1.4 | 1.8 | 3.0 | 3.2 |
| Benzene, 1,2,3,4-Tetramethyl- | 0.0 | 0.6 | 1.0 | 0.0 | 2.5 | 1.1 |

The aqueous fraction, which indicated deoxygenation by dehydration, increased with temperature. Also, coke and gas fractions increased progressively with temperature. CO₂ was the major gas product and made up between 53 and 83 wt% of the gas product indicating that deoxygenation also occurred through decarboxylation.

The organic distillate consisted of mainly aromatic hydrocarbons and a few aliphatic hydrocarbons. P-xylene, methyl benzene and tri- and tetramethylbenzenes were the major constituents. Elemental analysis of this product showed that high levels of deoxygenation occurred at temperatures of 370 °C and beyond.

4.4.2 Proposed Reaction Pathway for Acids and Esters

Two major reaction routes, occurring co-currently, are postulated for the conversion of propanoic acid. This is shown in Figure 4.29. One route (step 4) involves the decarboxylation of propanoic acid through cracking to produce carbon dioxide and hydrocarbon gases (mainly ethane). Decarboxylation has been mentioned [Kwart and King, 1969, Chen et al., 1989] to occur extensively with organic acids through oxygen removal as CO₂.

The second route (steps 1-3) results in the production of the main observed products; water, aromatic hydrocarbons and coke. According to this route, deoxygenation of propanoic acid (step 1) to produce long chain aldehydes and/or ketones and

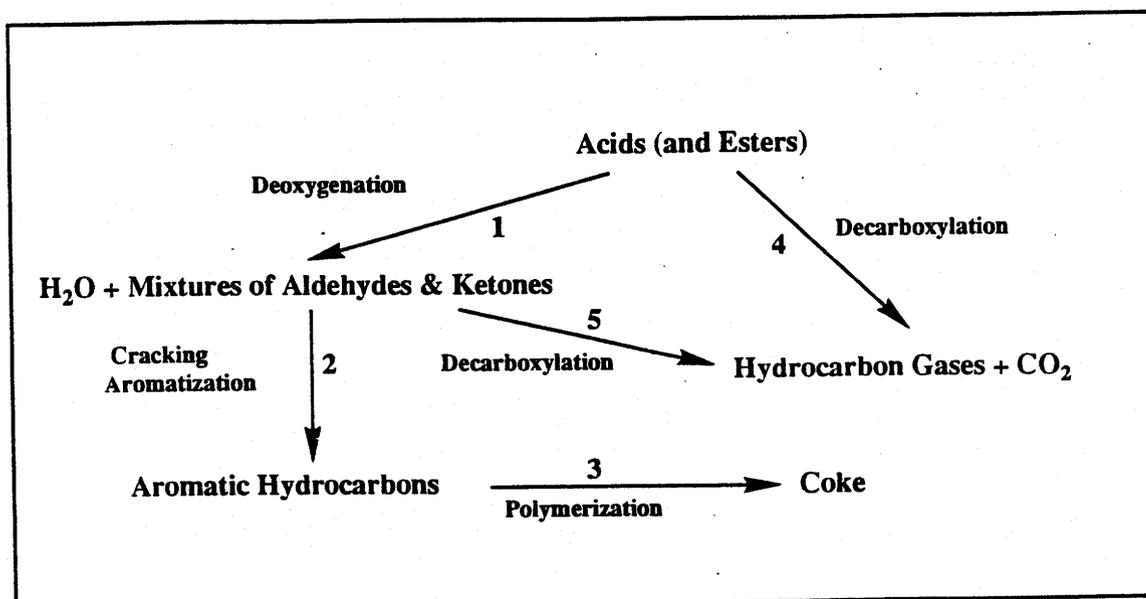


Figure 4.29 Reaction pathway for the conversion of acids and esters.

water was the first step. It has been mentioned [Diebold and Scahill, 1988] that compounds with carboxyl groups reject oxygen mainly as water and CO_2 over acid catalysts, the water being released through aldol condensation reactions [Chen et al., 1989]. Cracking of the alkyl groups off the main aldehyde or ketone molecules, followed by aromatization of the cracked fragments (step 2) then takes place. Subsequent alkylation followed by isomerization reactions involving the alkyl groups resulted in the formation of the alkylated benzenes. Polymerization (step 3) of the aromatic molecules followed by dehydrogenation of the polynuclear aromatics may result in coke formation [Pines, 1981, Guisnet et al., 1986]. Renaud et

al. [1988] mentions that the coking that results from upgrading of wood-oils can be linked to the high rates of polymerization /condensation reactions of acids in the gas phase.

4.4.3 Reactivity of Alcohols

4-methylcyclohexanol was used as a model compound to study the reactivity of alcohols over HZSM-5 catalyst. The reactivity data obtained from these runs are presented in Table 4.15. As can be seen, very high conversion were obtained at all temperatures and concentrations. Almost complete conversions were obtained at low concentrations and temperatures from 370 °C and beyond.

The yields of aqueous fraction, coke and gas increased monotonically with temperature indicating that these fractions could be part of the final products of the conversion process. The gas fraction consisted of C₁ to C₅+ hydrocarbon gases and carbon oxides; an indication of cracking and deoxygenation by the formation of carbon oxides. However, the major deoxygenation was though dehydration.

As shown by the elemental analysis (Table 4.15) of the organic distillate, alcohols are easily deoxygenated over HZSM-5 catalyst. For instance, even at temperatures as low as 330 °C, almost complete deoxygenation was achieved.

Table 4.15 continued.

Elemental Analyses of 4-Methylcyclohexanol and organic Distillate

| Element | Pure | 330 | 370 | 410 |
|------------------|------|------|------|-------|
| Carbon | 74.3 | 89.9 | 90.1 | 90.3 |
| Hydrogen | 12.0 | 10.0 | 9.5 | 9.7 |
| Oxygen | 25.7 | 0.1 | 0.4 | 0.0 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 |
| Deoxygenation, % | | 99.6 | 98.4 | 100.0 |

Yield of Major Conversion Compounds (wt% of Organic Distillate)

| CONCENTRATION, wt% | 100.0 | | | 17.0 | | |
|------------------------------------|-------|------|------|------|------|------|
| TEMPERATURE, °C COMPOUND | 330 | 370 | 410 | 330 | 370 | 410 |
| Hexane | 2.7 | 4.2 | 0.2 | 6.7 | 3.2 | 2.3 |
| Pentane, 3-ethyl- 2,2-dimethyl- | 0.5 | 0.4 | 0.1 | 1.1 | 0.6 | 0.1 |
| Benzene | 2.0 | 4.0 | 3.1 | 5.0 | 17.1 | 20.1 |
| Toluene | 13.0 | 22.5 | 6.9 | 18.8 | 22.5 | 12.7 |
| 1-Hexanol | 3.0 | 3.7 | 4.2 | 5.9 | 7.1 | 0.0 |
| Benzene, ethyl- | 12.9 | 19.8 | 17.7 | 22.8 | 17.8 | 6.5 |
| Cyclohexanol | 0.0 | 0.0 | 0.0 | 2.7 | 0.6 | 11.0 |
| P-Xylene | 3.3 | 5.7 | 7.4 | 2.0 | 4.1 | 27.5 |
| O-Xylene | 18.5 | 6.2 | 1.0 | 11.3 | 5.5 | 0.8 |
| 1-Heptanol | 2.2 | 2.6 | 0.2 | 0.8 | 2.2 | 0.0 |
| Benzene, 1,2,3,4- tetramethyl- | 1.9 | 0.3 | 2.3 | 0.0 | 0.1 | 1.2 |

Analysis of the organic distillate (Table 4.15) showed that it consisted of a large fraction of aromatic hydrocarbons, small fractions of aliphatic hydrocarbons and product alcohols. Methylbenzene, ethylbenzene and o- and p-xylenes were the major aromatic hydrocarbons. Hexane was the main aliphatic hydrocarbon produced, and 1-Heptanol and 1-Hexanol were the major product alcohols.

4.4.4 Proposed Reaction Pathway for Alcohols

The reaction pathway shown in Figure 4.30 is proposed for the conversion of methylcyclohexanol over HZSM-5. The main reaction route (steps 1-3) involves dehydration to yield water and a naphthene (methyl cyclohexene) as a first step. Dehydration of alcohols has been mentioned to be a major step in the reaction of ethanol over zeolites [Chen et al., 1989]. The dehydration may involve protonation of the alcohol to produce an intermediate cation, followed by release of water and a cyclohexene cation. Deprotonation of the cyclohexene cation takes place and terminates this step. The second step (step 2) involves a series of cationic dehydrogenations of the cyclohexene molecules by successive removal of hydrides by other cations to produce methylbenzene. Following the formation of methylbenzene, disproportionation, alkylation and isomerization reactions occurred. The disproportionation of methylbenzene produces benzene and dimethylbenzenes (xylenes) [Pines, 1981; Chen et al., 1989]. Chang [1983] also observed

from reactions of methanol over HZSM-5 catalyst that aromatization with hydrogen transfer was one of the major reaction steps.

Polymerization reactions of the aromatic rings lead to coke formation (step 3).

The second route (step 4) which may lead to the formation of hydrocarbon gases, carbon oxides and product alcohols involves the cracking or opening of the naphthenic ring to produce straight chain alcohols followed by cracking of some of the straight chain alcohols to produce a mixture of olefins, carbon oxides and alcohols. Some of the olefins may engage in M-2 forming reactions to produce BTX compounds and light paraffins [Chen and Yan, 1986].

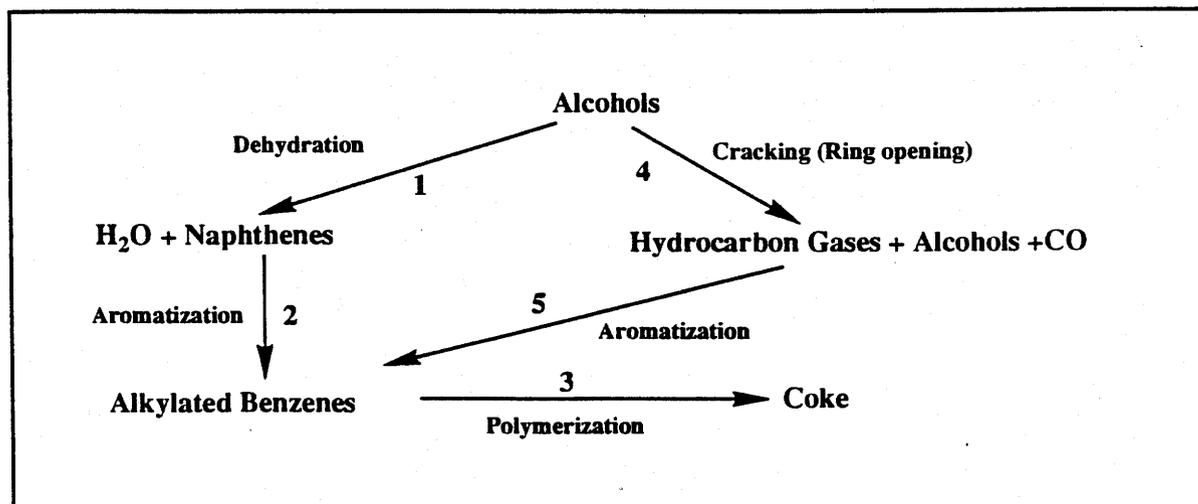


Figure 4.30 Reaction pathway for the conversion of alcohols.

4.5.5 Reactivity of Aldehydes and Ketones

The reactions of cyclopentanone and 2-methylcyclopentanone were used to study the reactivity of ketones and aldehydes over HZSM-5 catalyst. The detailed reactivity data for 2-methylcyclopentanone are presented in Table 4.16 and conversion versus temperature for 100 % cyclopentanone in Appendix D.8. For each concentration, the conversion increased with temperature and a decrease in concentration also favoured a conversion increase.

The high yields of aqueous fraction (Table 4.16) showed that deoxygenation by dehydration was a favourable step. Coke formation increased monotonically with temperature and again these products can be considered to be part of the final products of the conversion process. Gas formation also increased with temperature and consisted mainly of C_1 to C_5^+ hydrocarbon gases and carbon oxides (mainly carbon monoxide). Diebold and Scahill [1988] mentioned that decarbonylation of the carbonyl group over zeolite catalysts occurred largely as carbon monoxide.

The organic distillate (Table 4.16) consisted of mainly aromatic hydrocarbons, small fractions of aliphatic hydrocarbons and product aldehydes and ketones. Benzene, methylbenzene, p-xylene and 1,2,4-trimethylbenzene were the major aromatic hydrocarbon compounds produced.

Table 4.16
Reactivity data for 2-methylcyclopentanone.

Product Distribution and Conversion

| COMPOSITION, wt% | 100.0 | | | 36.6 | | |
|----------------------------------|-------|------|------|------|------|------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCT | | | | | | |
| Aqueous Fraction | 7.7 | 14.1 | 15.0 | 8.3 | 8.3 | 15.9 |
| Coke | 1.1 | 1.4 | 2.0 | 1.0 | 2.4 | 3.3 |
| Gas | 4.8 | 8.8 | 9.1 | 1.8 | 5.3 | 8.3 |
| Organic Distillate | 51.6 | 65.1 | 68.2 | 52.0 | 69.0 | 64.0 |
| Residue | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Unconverted methylcyclopentanone | 36.3 | 11.8 | 3.8 | 35.8 | 11.7 | 2.3 |
| Unaccounted Fraction | 1.6 | 1.3 | 1.4 | 0.9 | 0.8 | 1.2 |
| Conversion | 62.1 | 86.9 | 94.8 | 63.3 | 87.5 | 97.0 |

| COMPOSITION, wt% | 13.2 | | | 6.2 | | |
|----------------------------------|------|------|------|------|-------|------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCT | | | | | | |
| Aqueous Fraction | 7.3 | 8.5 | 12.5 | 6.9 | 8.1 | 11.8 |
| Coke | 1.7 | 2.8 | 6.6 | 2.5 | 4.1 | 8.0 |
| Gas | 2.1 | 9.5 | 16.4 | 2.5 | 11.4 | 18.8 |
| Organic Distillate | 63.8 | 68.2 | 61.6 | 68.3 | 67.6 | 59.1 |
| Residue | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Unconverted methylcyclopentanone | 23.7 | 7.8 | 1.4 | 18.4 | 7.3 | 1.0 |
| Unaccounted Fraction | 1.3 | 1.5 | 1.5 | 1.4 | 1.5 | 1.3 |
| Conversion | 75.0 | 88.9 | 97.1 | 80.3 | 91.20 | 97.7 |

Table 4.16 continued.

Elemental Analysis of 2-Methylcyclopentanone and Organic Distillate

| Element | Pure | 330 | 370 | 410 |
|------------------|------|------|------|------|
| Carbon | 67.5 | 67.8 | 77.2 | 89.2 |
| Hydrogen | 9.2 | 8.4 | 6.9 | 8.8 |
| Oxygen | 23.3 | 23.8 | 15.9 | 2.0 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 |
| Deoxygenation, % | | -1.0 | 31.8 | 91.4 |

Yield of Major Conversion Compounds (wt% of Organic Distillate)

| CONCENTRATION, wt% | 100.0 | | | 36.6 | | |
|------------------------------|-------|-------|-------|-------|-------|-------|
| TEMPERATURE, °C COMPOUND | 330.0 | 370.0 | 410.0 | 330.0 | 370.0 | 410.0 |
| Hexane | 1.7 | 1.6 | 1.5 | 1.9 | 1.4 | 1.8 |
| Benzene | 4.2 | 4.4 | 4.8 | 4.7 | 8.8 | 16.8 |
| Benzene, methyl- | 10.2 | 19.1 | 22.7 | 14.0 | 19.1 | 29.5 |
| 1,4-Hexadiene, 3-ethyl- | 0.0 | 0.2 | 3.8 | 0.2 | 0.0 | 0.0 |
| Benzene, ethyl- | 1.9 | 5.0 | 12.4 | 3.0 | 14.8 | 14.6 |
| p-Xylene | 11.0 | 14.6 | 6.1 | 2.4 | 11.9 | 3.7 |
| o-Xylene | 1.6 | 0.2 | 0.4 | 0.0 | 0.0 | 0.0 |
| Benzene, 1,2,4-trimethyl- | 3.5 | 6.3 | 5.8 | 4.9 | 2.3 | 2.5 |
| Cyclohexanone, 2,3-dimethyl- | 3.2 | 5.2 | 4.0 | 2.5 | 2.8 | 2.1 |
| Cyclooctane, 2-methyl- | 0.7 | 0.9 | 0.1 | 0.6 | 1.0 | 1.2 |
| Benzene, 1-propenyl- | 1.1 | 1.9 | 1.9 | 0.9 | 0.9 | 0.7 |

Hexane and 3-ethyl-1,4-hexadiene were the main aliphatic hydrocarbons and 2,3-dimethyl cyclohexanone was the main product ketone. The elemental analysis of the organic distillate (Table 4.16) showed that very high levels of deoxygenation occurred. As mentioned earlier, deoxygenation was through both dehydration and decarboxylation. Very high deoxygenation of cyclopentanone has also been reported by Dao et al. [1988] for cyclopentanone.

4.4.6 Proposed Reaction Pathway for Aldehydes and Ketones

Figure 4.31 shows the reaction pathway proposed to explain the reactivity of aldehydes and ketones over HZSM-5 catalyst. This scheme suggests that the first step of ketone or aldehyde conversion involves deoxygenation by dehydration to yield water and a naphthene (step 1). It has been mentioned [Chen et al., 1989] that two routes are possible in this case. The first is aldol condensation reaction involving an intermediate enol and a protonated carbonyl compound with subsequent removal of water [Wu, 1979] and bulking up of molecules. The second may involve the direct release of water and formation of a cyclopentene molecule from an intermediate enol molecule. It is not clear which route is most possible; however, considering the sizes of the transition complex and the final ketone molecule which may be formed through the aldol condensation route, it is likely that due to pore size constraints this may not be a preferred route.

The next sequence of steps (steps 2-3) involves cracking and aromatization to produce BTX compounds and light paraffins. Chen et al. [1989] mentions ring opening as the first step of the conversion of naphthenes to produce olefins. The resultant olefins undergo a series of M-2 forming reactions to produce BTX and light paraffins [Chen and Yan, 1986; Chen et al., 1989]. The M-2 forming reactions include cracking and oligomerization of the intermediate cyclopentene molecule to form a mixture of C₂ to C₁₀ olefins followed by hydrogen transfer, cyclization, alkylation and isomerization reactions. Benzene, alkylated benzenes and some paraffins are formed. Polymerization reactions of the aromatic rings also occur to produce coke (step 4).

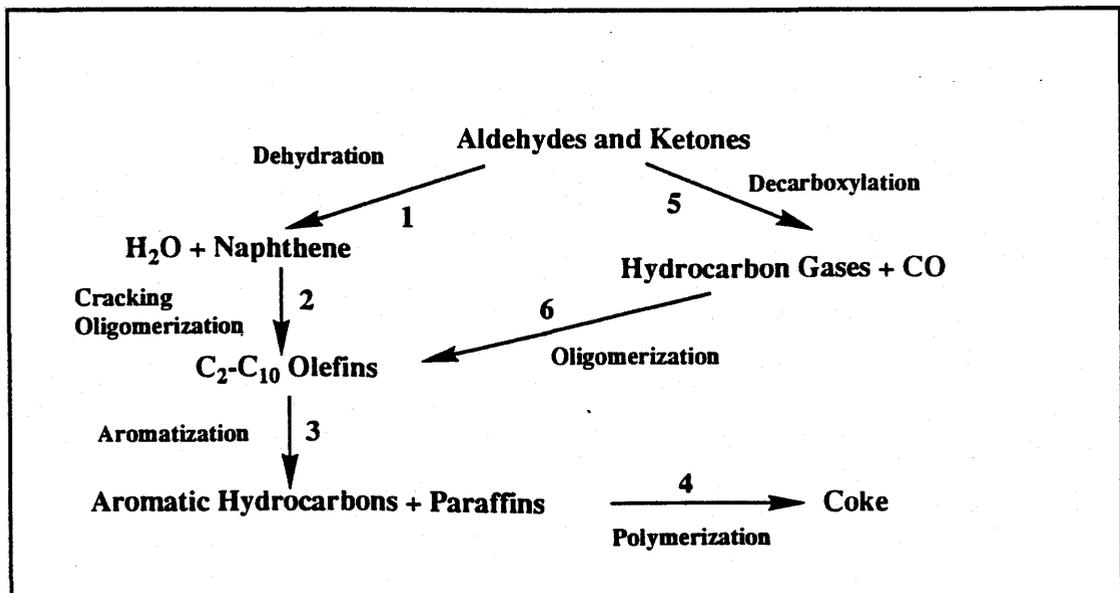


Figure 4.31 Reaction pathway for the conversion of aldehydes and ketones.

Decarbonylation through cracking of the ketone molecule may also occur leading to the observed carbon oxides (route 5). Dao et al. [1988] also noted that the main reaction of cyclopentanone conversion over ZSM-5 zeolite catalyst was thermal decarboxylation to give CO and C₄H₈ fragments that react further on the catalytic bed to produce aliphatic, aromatic and polyaromatic hydrocarbons.

4.4.7 Reactivity of Ethers

The reactions of methoxybenzene and ethoxybenzene were used to study the reactivity of ethers over HZSM-5 catalyst. The detailed reactivity data for ethoxybenzene are shown in Table 4.17. Appendix D.8 also includes the conversion with temperature for methoxybenzene in the pure state. The reactivity data show that the conversion generally increased when the concentration was decreased, but with temperature increase, a maximum was attained at 370 °C at all concentrations.

Only trace amounts of an aqueous fraction were obtained at all temperatures indicating that dehydration was difficult with ethers on HZSM-5 catalyst. Coke formation ranged between 0.8 to 2.8 wt% of the feed and increased with temperature. A high gas production was attained at all temperatures. Analysis of this gas fraction showed that it was predominantly hydrocarbon gases.

Table 4.17
Reactivity data for ethoxybenzene.

Product Distribution and Conversion

| COMPOSITION, wt% | 100.0 | | | 43.0 | | |
|----------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCT | | | | | | |
| Aqueous Fraction | Trace | Trace | Trace | Trace | Trace | Trace |
| Coke | 0.8 | 2.4 | 2.8 | 0.6 | 1.9 | 5.6 |
| Gas | 23.7 | 23.7 | 23.7 | 17.9 | 18.5 | 21.6 |
| Organic Distillate | 17.0 | 25.0 | 22.8 | 29.0 | 33.3 | 20.9 |
| Residue | 0.3 | 0.4 | 0.5 | Trace | 0.6 | 0.9 |
| Unconverted Ethoxybenzene | 57.1 | 47.6 | 49.0 | 51.7 | 44.5 | 49.9 |
| Unaccounted Fraction | 1.1 | 0.9 | 1.2 | 0.8 | 1.2 | 1.1 |
| Conversion | 41.8 | 51.7 | 49.9 | 47.5 | 54.3 | 49.0 |

| COMPOSITION, wt% | 12.6 | | | 4.8 | | |
|----------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCT | | | | | | |
| Aqueous Fraction | Trace | Trace | Trace | Trace | Trace | Trace |
| Coke | 0.8 | 4.1 | 6.4 | 1.0 | 4.8 | 6.8 |
| Gas | 14.6 | 14.6 | 15.5 | 13.8 | 14.7 | 14.9 |
| Organic Distillate | 34.7 | 37.4 | 26.8 | 46.3 | 41.6 | 26.6 |
| Residue | Trace | Trace | Trace | Trace | Trace | Trace |
| Unconverted Ethoxybenzene | 48.8 | 43.0 | 50.3 | 38.0 | 38.0 | 50.5 |
| Unaccounted Fraction | 1.1 | 0.9 | 1.2 | 1.0 | 0.9 | 1.2 |
| Conversion | 50.1 | 56.1 | 48.5 | 61.0 | 61.1 | 48.3 |

Table 4.17 continued.

Elemental Analysis of Ethoxybenzene and Organic Distillate

| Element | Pure | 330 | 370 | 410 |
|------------------|------|------|------|------|
| Carbon | 75.6 | 76.7 | 79.0 | 75.7 |
| Hydrogen | 7.4 | 7.7 | 8.4 | 8.0 |
| Oxygen | 17.0 | 15.4 | 12.6 | 16.3 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 |
| Deoxygenation, % | | 9.6 | 26.3 | 4.2 |

Yield of Major Conversion Compounds (wt% of Organic Distillate)

| COMPOSITION, wt% | 100.0 | | | 43.0 | | |
|----------------------------------|-------|-----|-----|------|------|------|
| | 330 | 370 | 410 | 330 | 370 | 410 |
| TEMPERATURE, °C | | | | | | |
| COMPOUND | | | | | | |
| Benzene, methyl- | 0.1 | 0.2 | 0.7 | 1.1 | 0.9 | 0.7 |
| Benzene, ethyl- | 0.2 | 0.2 | 0.9 | 1.0 | 1.7 | 1.3 |
| Phenol | 0.9 | 0.9 | 1.0 | 1.3 | 2.1 | 1.3 |
| Benzene, 1-ethoxy-4-methyl- | 0.7 | 0.3 | 0.7 | 1.3 | 1.1 | 0.6 |
| Phenol, 2-methyl- | 1.0 | 0.9 | 0.7 | 1.2 | 0.9 | 0.0 |
| Phenol, 4-methyl- | 1.0 | 1.1 | 0.9 | 0.6 | 0.0 | 0.0 |
| Benzofuran, 2-methyl- | 3.0 | 4.6 | 3.8 | 5.4 | 2.5 | 1.3 |
| Benzene, 1-methoxy-1-propenyl)- | 5.6 | 6.8 | 6.1 | 5.6 | 20.5 | 16.8 |
| Benzene, (3-methoxy-1-propenyl)- | 3.1 | 4.2 | 7.2 | 4.9 | 1.9 | 1.0 |
| Phenol, 2,5-dimethyl- | 1.0 | 2.1 | 1.4 | 0.8 | 1.9 | 1.1 |

Only trace carbon oxides were measured. Since gas production was significantly high, it can be said that this was one of the major routes of the conversion process.

Small fractions of non-volatile residue were also produced, indicating that some of the reactions favoured the formation of high non-volatile molecules.

The organic distillate (Table 4.17) consisted of various alkylated phenols, oxygenated aromatics and small fractions of hydrocarbons (up to 3 wt%). The alkylated phenols consisted of mainly mono- and dimethyl phenols. A number of alkoxybenzene compounds such as 1-methoxy-1-propenyl benzene, 1-ethoxy-4-methylbenzene and a few alkylated benzofurans made up the oxygenated aromatic fraction. Elemental analysis of the organic distillate showed that it was highly oxygenated. The low levels of deoxygenation may be due to the stable nature of the aromatic ether molecule. It is generally understood that ethers are difficult to react [Morrison and Boyd, 1966].

4.4.8 Proposed Reaction Pathway for Ethers

The conversion of ethers are proposed to proceed through two reaction routes occurring co-currently. This is shown in Figure 4.32. One route (step 1) suggests an initial disproportionation-type reaction of the alkoxybenzene molecule followed by cracking (step 2) to produce other ethers and hydrocarbon gases. The disproportionation of alkoxybenzene could yield a phenol and another alkoxybenzene molecule with

larger alkyl groups. The phenol molecule formed can undergo two types of reactions. The first involves a condensation reaction with another alkoxybenzene molecule to produce water and a high molecular weight ether followed by a further condensation to produce larger molecules with high boiling points. This may explain the residue or coke formation.

Condensation reactions of the original alkoxybenzene molecule (Step 6) may also occur to produce residue or coke. However, the trace amounts of water and low yields of coke and residue show that the extent of these reactions are rather minor.

The large alkyl chains on the ether groups formed in step 1 may crack off producing alkenes and various oxygenated aromatic compounds (step 2). These alkenes may alkylate phenols (second reactions of phenols) (step 3) or result in the formation of hydrocarbon gases.

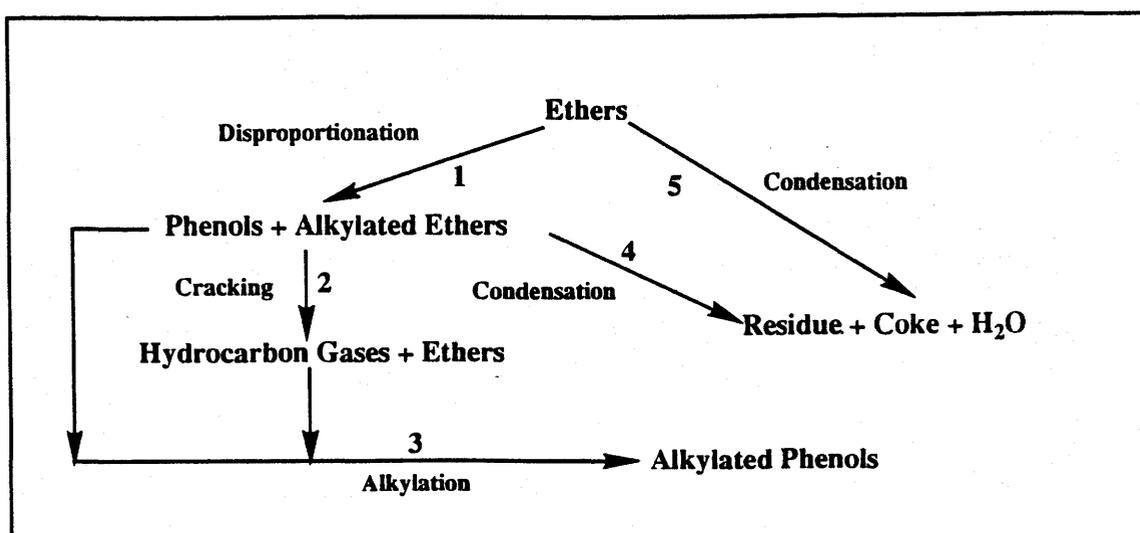


Figure 4.32 Reaction pathway for the conversion of ethers.

4.5.9 Reactivity of Phenols of Substituted Phenols

Phenols make up about 28 wt% of the organic volatile fraction and is the most abundant oxygenate present in the wood-oil. In this work, the reactivity of phenol over HZSM-5 was first studied. Conversion was a maximum of 9.3 % at 370 °C (Appendix D.8) when a 15 wt% concentration of phenol was used. At higher phenol concentrations, conversions were always far less than 10%. Phenols are understood to have low conversion rates due to the stable nature of the phenol molecule [Evans and Milne, 1988]. In the wood-oil, phenols occur in various forms including alkylated and alkoxy derivatives. To completely understand the reactivity of these substituted phenols, eugenol was selected and studied. Eugenol was the one major component identified in the volatile fraction of the wood-oil (Table 4.2). Table 4.18 presents the reactivity data for eugenol. As can be seen, conversion generally increased with increase in temperature and a decrease in concentration.

Small yields of an aqueous fraction were produced. The yields of aqueous fraction, coke and gas fractions increased monotonically with temperature. The gas produced contained mainly C₁ to C₅⁺ hydrocarbon gases and trace amounts of carbon oxides, thus showing that the formation of carbon oxides was not a major route to deoxygenation of phenols.

Table 4.18
Reactivity data for 2-methoxy-4-(propenyl) phenol (Eugenol).

Product Distribution and Conversion

| COMPOSITION, wt% | 100.0 | | | 43.0 | | |
|---------------------|-------|------|------|-------|------|------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCT | | | | | | |
| Aqueous Fraction | Trace | 1.1 | 1.9 | 0.6 | 1.2 | 2.5 |
| Coke | 1.6 | 2.4 | 4.0 | 1.2 | 3.1 | 4.1 |
| Gas | 0.3 | 1.1 | 2.1 | Trace | 1.8 | 3.7 |
| Organic Product | 5.0 | 5.3 | 7.8 | 7.1 | 7.3 | 7.8 |
| Residue | 2.1 | 2.6 | 4.0 | 0.4 | 0.6 | 1.8 |
| Unconverted Eugenol | 42.0 | 34.7 | 38.0 | 46.1 | 37.5 | 46.9 |
| Unaccounted | 1.2 | 2.1 | 1.9 | 1.5 | 1.7 | 2.1 |
| Conversion | 56.8 | 63.3 | 60.1 | 52.4 | 60.8 | 51.0 |

| COMPOSITION, wt% | 10.7 | | | 6.2 | | |
|---------------------|-------|-------|-------|-------|-------|-------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCTS | | | | | | |
| Aqueous Fraction | Trace | Trace | Trace | Trace | Trace | Trace |
| Coke | 2.4 | 4.9 | 5.3 | 2.6 | 3.2 | 5.8 |
| Gas | Trace | 2.4 | 4.9 | Trace | 2.9 | 4.1 |
| Organic Product | 7.4 | 7.3 | 10.7 | 7.4 | 8.8 | 11.8 |
| Residue | Trace | Trace | 0.6 | Trace | Trace | Trace |
| Unconverted Eugenol | 49.2 | 39.0 | 20.5 | 37.2 | 40.6 | 13.9 |
| Unaccounted | 1.6 | 1.8 | 1.8 | 1.4 | 2.1 | 1.9 |
| Conversion | 49.2 | 59.3 | 77.7 | 51.4 | 57.3 | 84.3 |

Table 4.18 continued.

Elemental Analysis of Eugenol and Organic Distillate

| Element | Pure | 330 | 370 | 410 |
|------------------|------|------|------|------|
| Carbon | 72.4 | 72.9 | 73.2 | 73.4 |
| Hydrogen | 7.0 | 7.9 | 7.6 | 8.1 |
| Oxygen | 20.5 | 19.1 | 19.2 | 18.5 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 |
| Deoxygenation, % | | 6.7 | 6.7 | 9.8 |

Yield of Major Conversion Compounds (wt% of Organic Distillate)

| CONCENTRATION, wt% | 100% | | | 43.0 | | |
|------------------------------|-------|-------|-------|-------|-------|-------|
| TEMPERATURE, °C COMPOUND | 330.0 | 370.0 | 410.0 | 330.0 | 370.0 | 410.0 |
| Benzene, (1-methylethyl)- | 0.1 | 0.3 | 0.5 | 0.1 | 0.2 | 0.5 |
| Benzene, 1-ethenyl-2-methyl- | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.3 |
| Phenol, 2-methyl- | 0.3 | 0.2 | 0.2 | 0.3 | 0.2 | 0.0 |
| Benzofuran, 2-methyl- | 0.0 | 0.1 | 1.0 | 0.5 | 0.3 | 0.5 |
| Phenol, 2,5-dimethyl- | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.1 |
| Phenol, 2-methoxy-4-methyl- | 0.2 | 0.3 | 0.8 | 0.3 | 0.5 | 0.7 |
| 1,3-Benzenediol | 0.2 | 0.3 | 0.4 | 0.5 | 0.3 | 0.4 |
| Eugenol isomers | 49.2 | 49.4 | 31.8 | 41.0 | 47.6 | 31.5 |
| Benzofuran, 4,7-dimethyl- | 0.1 | 0.2 | 0.3 | 0.4 | 0.8 | 0.4 |

Residue formation also increased with temperature. The production of this fraction was an indication that certain reactions led to the production of larger molecules which were non-volatile components and that it was favoured by a temperature increase.

The organic distillate (Table 4.18) consisted predominantly of various isomers of eugenol, i.e., (2-methoxy-4-(2-propenyl) phenol). Some of these isomers were 2-methoxy-5-(1-propenyl) phenol, 2-methoxy-4-(1-propenyl) phenol, 2-methoxy-4-(1-propenyl) phenol. As can be seen, small yields of alkylated phenols, aliphatic and aromatic hydrocarbons and other oxygenated aromatics such as ethers, alkylated benzofuran and benzenediol, were also identified.

4.4.10 Proposed Reaction Pathway for Substituted Phenols

Figure 4.33 shows the reaction pathway proposed for the reaction of substituted phenols. As mentioned above, the major products were isomers of the phenol showing that isomerization of the original molecule was the main reaction route. Isomerization of substituted phenols have been mentioned to be one of the major reactions of phenols over zeolite catalysts [Renaud et al., 1986; Chen et al., 1989]. It appears that isomerization was a much easier reaction route compared to reactions routes.

The second reaction route occurring to a far lesser extent involves condensation-type reactions which resulted in aqueous

fraction and high boiling point molecules, mainly ethers. It has been mentioned [Chantal et al., 1985] that the dehydration of phenol leads to an intermediate ether formation. Successive condensation may result in non-volatile residue or coke.

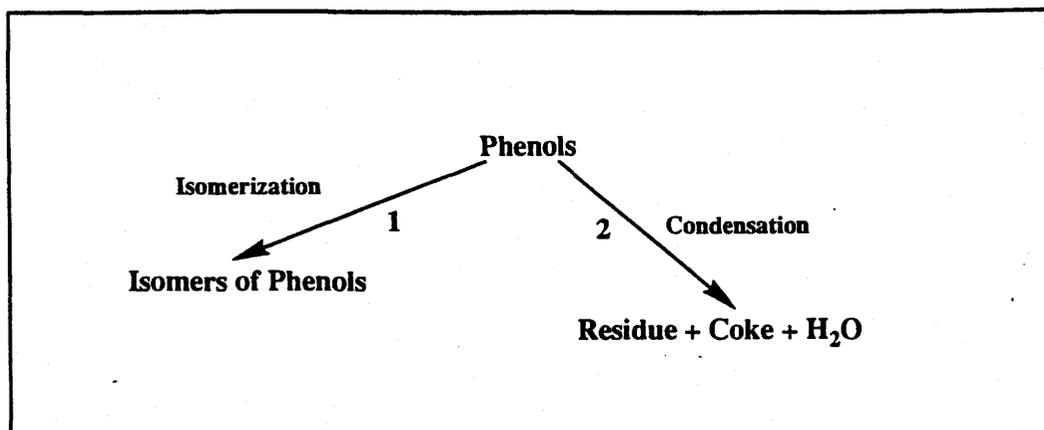


Figure 4.33 Reaction pathway for the conversion of phenols.

4.4.11 Reactivity of Synthetic and Wood-oil Volatiles

In the previous sections, the study of individual model compounds representing the chemical groups was conducted. Also, in the literature individual model compounds have been studied. However, it is well known that the reactivity behaviour of most compounds do change in the presence of other reactants due to synergistic effects of the reactants and/or products. Studying model compounds alone therefore can only provide partial information on the actual reactivity behaviour of the chemical groups or the wood-oil. Information involving mixtures of model compounds are lacking. As a result, in the current work, first, a study was carried out whereby the reactivity of a mixture of the model compounds was studied. This mixture (termed synthetic volatile) was prepared by combining the model compounds in the proportion in which the chemical groups to which they belong occurred in the wood-oil volatiles. Following this, the reactivity of wood-oil volatiles was studied. The reactivity data from studying the synthetic volatiles are presented in Table 4.19, and for wood-oil volatiles in Table 4.20.

Synthetic Volatiles

The results (Table 4.19) show that the conversion increased with temperature and also increased as the concentration was decreased. These conversions were calculated based on the conversions of the individual compounds. The

product distribution also included an aqueous fraction, coke, gas, residue and organic distillate. Again, the formation of an aqueous fraction meant deoxygenation by dehydration. This fraction increased with temperature. Also, the coke and gas fractions increased with temperature. Following the analysis of the reaction of individual compounds, it appears that dehydration occurred through either aldol condensation or acid catalyzed reactions of hydroxyl groups; coke through polymerization of aromatic hydrocarbons and polymerization and condensation of oxygenated aromatics. The gas fraction which consisted of C_1 to C_5+ hydrocarbon gases and carbon oxides formed through cracking and oligomerization reactions. Residue formation was shown to be the result of polymerization and condensation reactions of ethers and phenols. It also increased with temperature.

The most striking observation was the increased reactivity of the individual compounds in the mixture compared to when the compounds were studied separately. For instance, the conversion of phenols in the mixture increased compared to when treated as a single feed pointing to a complex reaction behaviour which may involve synergism between reactants and products.

Table 4.19
Reactivity data for synthetic volatiles.

Product Distribution and Conversion

| COMPOSITION, wt% | 100.0 | | | 41.0 | | |
|----------------------|-------|-------|-------|-------|-------|-------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCT | | | | | | |
| Aqueous Fraction | 0.0 | 1.2 | 4.0 | 0.0 | 0.0 | 2.9 |
| Coke | 2.4 | 7.3 | 12.1 | 2.1 | 4.4 | 8.1 |
| Gas | 2.8 | 5.5 | 10.7 | 3.8 | 6.7 | 12.3 |
| Organic Distillate | 62.7 | 61.6 | 52.6 | 71.6 | 64.1 | 64.2 |
| Residue | Trace | 3.8 | 6.5 | Trace | 1.8 | 3.3 |
| Unconverted Reactant | 31.4 | 19.8 | 13.1 | 21.8 | 9.5 | 8.5 |
| Unaccounted | 0.8 | 0.8 | 1.1 | 0.8 | 1.1 | 0.8 |
| Conversion | 67.8 | 72.4 | 85.9 | 77.4 | 89.4 | 90.7 |
| COMPOSITION, wt% | 23.0 | | | 12.0 | | |
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| PRODUCT | | | | | | |
| Aqueous Fraction | Trace | Trace | Trace | Trace | Trace | Trace |
| Coke | 1.1 | 4.2 | 6.8 | 1.0 | 4.3 | 5.5 |
| Gas | 4.3 | 8.1 | 13.8 | 4.1 | 8.0 | 14.0 |
| Organic Distillate | 86.7 | 82.1 | 73.7 | 89.8 | 84.5 | 78.1 |
| Residue | Trace | 0.6 | 1.6 | Trace | Trace | 0.5 |
| Unconverted Reactant | 6.7 | 3.9 | 3.4 | 4.0 | 2.1 | 0.8 |
| Unaccounted | 1.1 | 1.1 | 0.8 | 1.1 | 1.1 | 1.1 |
| Conversion | 92.2 | 95.0 | 95.9 | 94.9 | 96.8 | 98.1 |

Table 4.19 continued.

Elemental Analysis of Synthetic Volatiles and Organic Distillate

| Element | Pure | 330 | 370 | 410 |
|------------------|------|------|------|------|
| Carbon | 72.5 | 76.7 | 77.7 | 79.2 |
| Hydrogen | 8.1 | 6.4 | 6.7 | 8.3 |
| Oxygen | 19.4 | 16.9 | 15.6 | 12.5 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 |
| Deoxygenation, % | | 12.9 | 19.6 | 35.6 |

Yield of Major Conversion Compounds (wt% of Organic Distillate)

| CONCENTRATION, wt% | 100.0 | | | 41.0 | | |
|-----------------------------------|-------|-----|-----|------|------|------|
| | 330 | 370 | 410 | 330 | 370 | 410 |
| TEMPERATURE, °C | | | | | | |
| COMPOUND | | | | | | |
| Benzene | 1.2 | 1.9 | 3.6 | 1.6 | 12.0 | 8.4 |
| Benzene, methyl- | 4.4 | 2.8 | 7.6 | 3.5 | 10.5 | 10.5 |
| Benzene, ethyl- | 0.5 | 1.1 | 2.4 | 1.1 | 2.4 | 4.2 |
| o-Xylene | 1.2 | 2.6 | 5.9 | 2.3 | 5.2 | 8.4 |
| Benzene, 1,2,3-trimethyl- | 2.3 | 3.4 | 2.2 | 3.2 | 6.2 | 4.6 |
| Benzene, 1-propenyl- | 0.2 | 0.2 | 0.0 | 0.4 | 0.0 | 0.7 |
| Benzene, 1-ethoxy-3-methyl- | 0.5 | 0.2 | 0.1 | 0.0 | 1.1 | 1.1 |
| Phenol, 2-methyl- | 0.0 | 0.0 | 0.5 | 0.9 | 2.1 | 4.0 |
| Benzene, (3-methoxy, 1-propyl)- | 8.9 | 9.7 | 4.4 | 2.1 | 0.5 | 2.8 |
| Phenol, 2,5-dimethyl- | 0.1 | 0.3 | 0.6 | 1.1 | 0.0 | 3.0 |
| Phenol, 2-methoxy-5-(1-propenyl)- | 2.5 | 2.4 | 1.7 | 3.4 | 3.5 | 3.4 |

Wood-oil Volatiles

Since this mixture contained over 80 compounds, it was not possible to trace the conversion of the individual compounds. As a result, no conversion versus temperature data were calculated. However, the product distribution and elemental analysis were measured (Table 4.20). Here also, the products consisted of an aqueous fraction, coke, gas, residue and organic distillate. Similar deductions can be made for aqueous, coke, gas and residue fractions as with the synthetic volatiles.

However, profound differences existed between the organic distillate products from synthetic and wood-oil volatiles. First, deoxygenation was very high, 71 to 88 % compared to 13 to 35 % with synthetic volatiles. This may be explained by the increased reactivity of the individual compounds due to the low concentrations compared to their concentrations in the synthetic volatiles. Also, the interaction effect of the other reactants and products may have enhanced the reactivity of the individual components. The increased reactivity may have resulted in the production of a higher quality organic distillate, i.e., high hydrocarbon formation and low oxygen content, compared to the synthetic volatiles.

Secondly, higher yields of aromatic hydrocarbons were obtained compared to the reactivity of synthetic volatiles (Tables 4.19 and 4.20). Analysis of the organic distillate showed that high yields of aromatic hydrocarbons, typically

Table 4.20 continued.

Elemental analysis of Wood-oil Volatiles and Organic Distillate

| Element | Pure | 330 | 370 | 410 |
|------------------|------|------|------|------|
| Carbon | 68.0 | 88.4 | 88.7 | 88.9 |
| Hydrogen | 9.2 | 5.1 | 6.1 | 8.6 |
| Oxygen | 22.4 | 6.5 | 5.2 | 2.5 |
| Nitrogen | 0.0 | 0.0 | 0.0 | 0.0 |
| Deoxygenation, % | | 71.0 | 76.8 | 88.8 |

Yield (wt%) of Major Conversion Compounds of Organic Distillate

| CONCENTRATION, wt% | 100.0 | | | 44.0 | | |
|---------------------------|-------|------|------|------|------|------|
| TEMPERATURE, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| COMPOUND | | | | | | |
| Hexane | 1.3 | 0.9 | 0.9 | 2.0 | 1.1 | 0.8 |
| Benzene | 1.8 | 5.0 | 7.8 | 14.1 | 23.7 | 26.8 |
| Benzene, methyl- | 9.0 | 18.1 | 16.4 | 9.8 | 12.5 | 14.4 |
| Benzene, ethyl- | 2.9 | 5.8 | 6.3 | 4.3 | 5.4 | 6.0 |
| P-xylene | 11.4 | 17.0 | 13.1 | 8.7 | 9.5 | 10.6 |
| O-xylene | 2.0 | 3.9 | 0.5 | 1.9 | 2.4 | 2.7 |
| Benzene, 1,2,4-trimethyl- | 2.8 | 3.8 | 0.5 | 1.2 | 0.5 | 2.0 |
| Benzene, 1,2,3-trimethyl- | 3.5 | 2.3 | 0.9 | 2.5 | 1.1 | 1.0 |
| Benzene, (1-methylethyl)- | 2.3 | 4.3 | 2.2 | 1.8 | 2.1 | 2.7 |
| 1H-Indene | 0.7 | 0.9 | 1.4 | 0.3 | 0.2 | 0.7 |
| 1H-Indene, 1-ethylidene | 1.3 | 0.3 | 0.6 | 1.1 | 0.2 | 0.0 |

benzene and alkylated benzenes, were obtained. Alkylated phenols were the next single component identified in high amounts.

4.4.12 Proposed Reaction Pathway for Wood-oil Volatiles

Following the study on the model compounds, synthetic volatiles and wood-oil volatiles, a possible reaction pathway was proposed. This is shown in Figure 4.34. According to this scheme, the first reaction route involves deoxygenation and cracking (step 1). Deoxygenation occurs through dehydration and cracking produces further deoxygenation through decarboxylation. Following the initial deoxygenation, secondary cracking occurred resulting in the formation of olefins and oxygenates. Oligomerization of olefins produces a mixture of C₂ to C₁₀ olefins (step 2). The next step (3) involves a series of aromatization reactions which may include hydrogen transfer and cyclization followed by alkylation and isomerization to form benzene and alkylated benzenes. Also, alkylation and isomerization of phenol may occur to form various alkyl substituted phenols.

This scheme also notes that coke and residue formation occurs through dual reactions of polymerization of aromatic hydrocarbons (step 4) and polymerization/condensation reactions of oxygenated compounds (step 5).

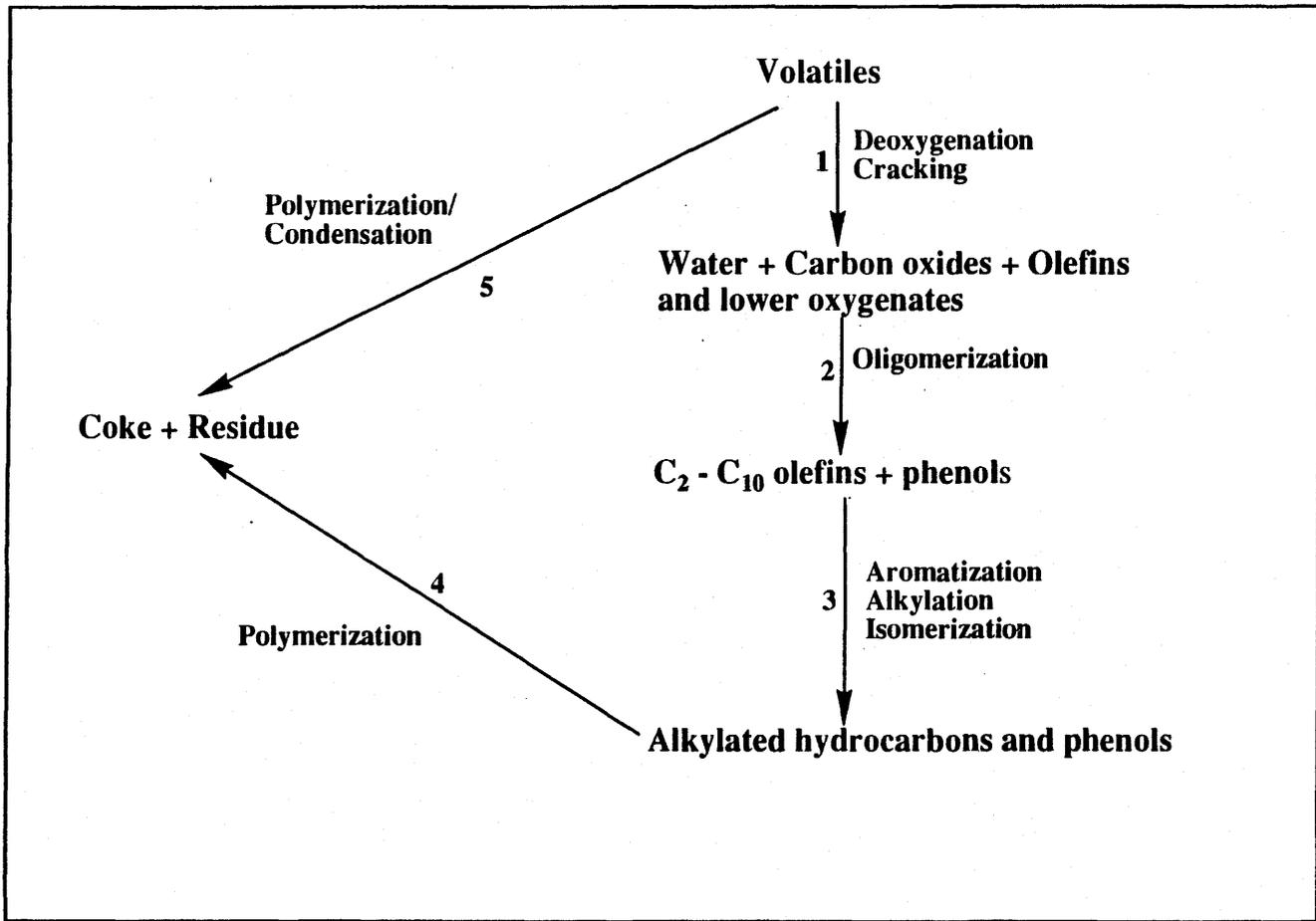


Figure 4.34 Reaction pathway for the conversion of wood-oil volatile fraction.

4.4.13 Proposed Reaction Pathway for Conversion of Whole Wood-oil

In section 4.2 it was shown that by fractionation, the wood-oil could be separated into volatile and non-volatile fractions, and that it was composed of various chemical groups. In the preceding sections, the reactivity of the chemical groups through model compound reactions was studied. The reactivity of the wood-oil components in increasing complexity through synthetic mixtures and the actual wood-oil volatiles was also studied. Reaction pathways were proposed for the chemical groups and subsequently for the wood-oil volatiles. In this section, information from these studies is combined with information on the reactivity data for the whole wood-oil from section 4.3 to propose reaction pathway(s) for the conversion of the wood-oil.

So far, the only portion of the wood-oil unaccounted for was the non-volatile fraction. It was presumed that there are two reaction routes through which this fraction could react. The first is cracking to form an intermediate volatile or gas product and the second involves polymerization to form residue and/or coke.

Following the discussion presented above, two reaction pathways (Figure 4.35 and 4.36) are proposed for the conversion of the wood-oil. In both pathways the wood-oil is initially separated into volatile and non-volatile fractions as soon as reaction temperatures are encountered

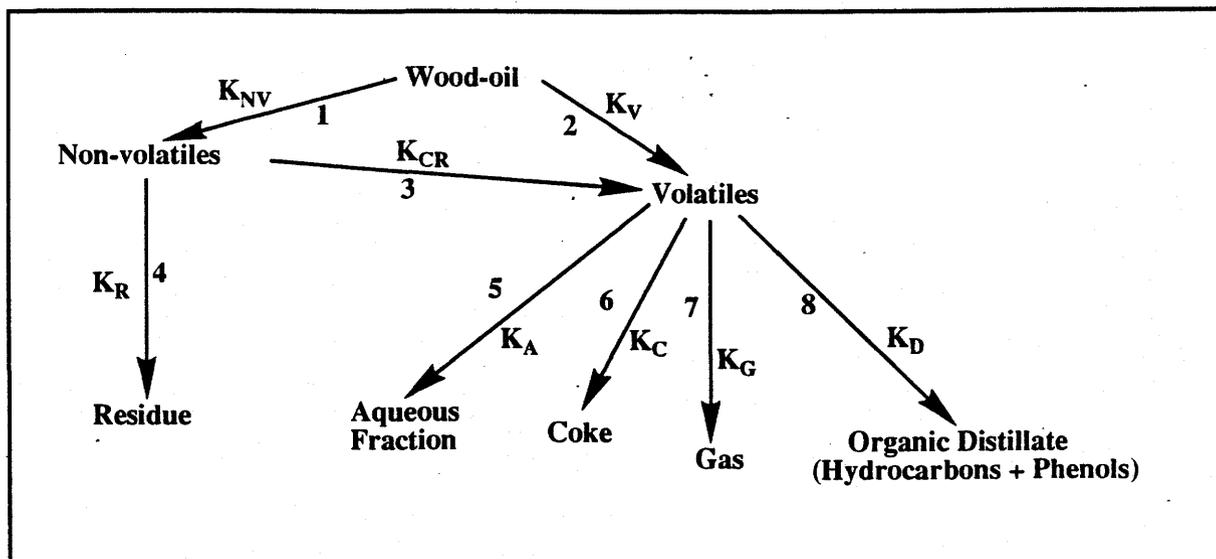


Figure 4.35 Reaction pathway for the conversion of wood-oil (Model I).

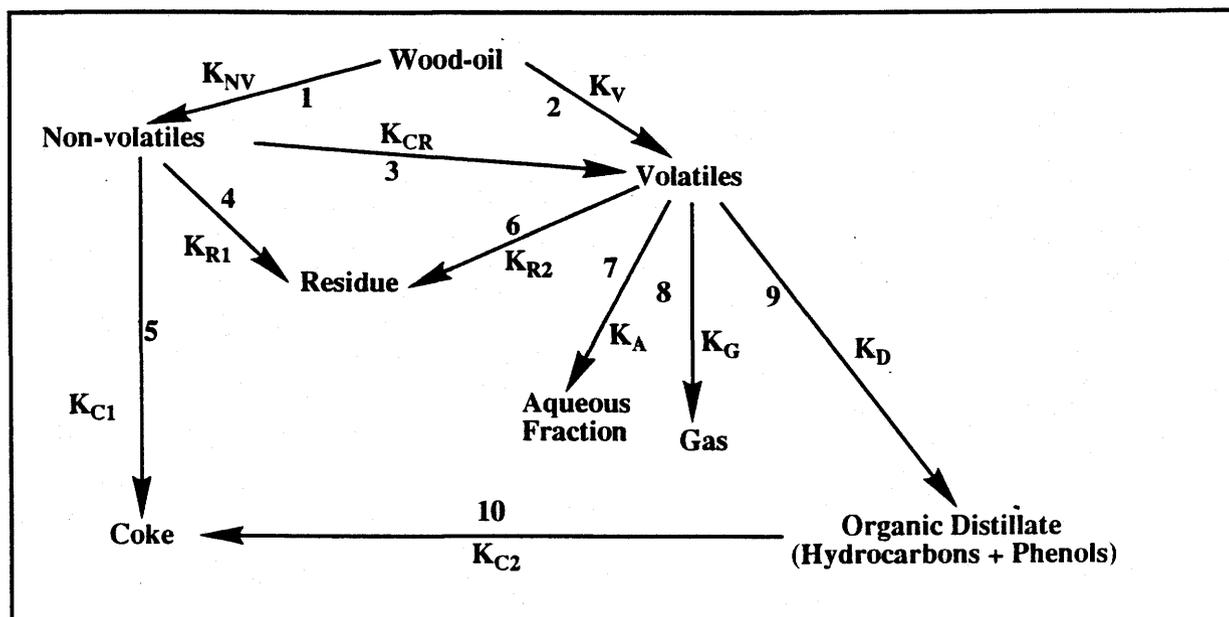


Figure 4.36 Reaction pathway for the conversion of wood-oil (Model II).

(steps 1 and 2). Model I proposes that the non-volatiles reacted to form mainly volatiles and non-volatile residue whereas model II proposes that in addition to the volatile and residue formation, some of the non-volatile components polymerized on the catalyst to form coke.

According to both models, the volatile portion reacts through deoxygenation, secondary cracking, oligomerization, olefin formation, hydrogen transfer, cyclization, disproportionation, alkylation and isomerization reactions to form the hydrocarbon-rich product (organic distillate). Polymerization and condensation reactions of some aromatic oxygenates and hydrocarbons result in coke formation. Also, deoxygenation through dehydration results in water formation and decarboxylation lead to the production of carbon oxides. The hydrocarbon gases are formed from cracking reactions. In addition to these, model II further suggests that some of the volatiles react to form the residue which model I does not account for.

In summary, it has been shown that to produce the hydrocarbon-rich fraction from wood oil, three sets of reactions must occur:

1. Primary reactions; consisting of mostly cracking and deoxygenation reactions.
2. Secondary reactions; consisting of secondary cracking, oligomerization, olefin formation, hydrogen transfer and cyclization reactions.

3. Terminal or terminating reactions; consisting of alkylation, isomerization, disproportionation and polymerization reactions.

4.5 Phase 6: KINETIC MODELING II: CHEMICAL KINETICS, PARAMETER ESTIMATION AND MODEL DERIVATION AND PREDICTION

The objectives of this part of the research was to derive a mathematical model that best predicted the yields of products from the conversion of wood-oil over HZSM-5 catalyst and also to discriminate between the two rival reaction pathways of Figures 4.35 and 4.36. It consisted of a theoretical and an experimental section. The theoretical section was made up of the following;

1. Derivation of rate models (chemical kinetics).
2. Derivation of product prediction models.
3. Kinetic parameter estimation.
4. Model prediction of yields of products and comparison with experimental results obtained from upgrading the wood-oil (section 4.2).
5. Derivation of hydrocarbon selectivity relations.

The experimental section was designed to collect rate-concentration data. This has been described in chapter 3.

4.5.1 Rate models

The following rate models (with initial conditions) were derived for each component based on the two reaction pathways

shown in Figure 4.35 (Model I) and 4.36 (Model II). Each path is described by the rate which depends on the temperature (T), concentration (C), and the kinetic parameters, K_i , (reaction rate constant); E_i , (activation energy) and a_i , (order of reaction). The rate models were derived based on the power law assumption.

1. Rate of formation of non-volatiles

Model 1:

$$r_{NV} = \frac{dC_{NV}}{dt} = K_{NV} C_W^{b_1} - K_R C_{NV}^I - K_{Cr} C_{NV}^{Cr} \quad (4.2)$$

Model 2:

$$r_{NV} = \frac{dC_{NV}}{dt} = K_{NV} C_W^{b_1} - K_{R_1} C_{NV}^I - K_{Cr} C_{NV}^{Cr} - K_{C_1} C_{NV}^{C_1} \quad (4.3)$$

Initial condition: $t=0$, $C_{NV}=0$.

2. Rate of formation of volatiles

Model 1:

$$r_V = \frac{dC_V}{dt} = K_V C_W^{b_2} + K_{Cr} C_{NV}^{Cr} - K_D C_V^d - K_W C_V^w - K_G C_V^g - K_C C_V^c \quad (4.4)$$

Model 2:

$$r_V = \frac{dC_V}{dt} = K_V C_W^{b_2} + K_{Cr} C_{NV}^{Cr} - K_D C_V^d - K_W C_V^w - K_G C_V^g - K_{C_2} C_V^{C_2} - K_{R_2} C_V^{I_2} \quad (4.5)$$

Initial condition: $t=0$, $C_V=0$.

3. Rate of formation of organic distillate

Models 1 and 2:

$$r_D = \frac{dC_D}{dt} = K_D C_V^d \quad (4.6)$$

Initial condition: $t=0$, $C_D=0$.

4. Rate of formation of aqueous fraction

Models 1 and 2:

$$r_A = \frac{dC_A}{dt} = K_A C_V^a \quad (4.7)$$

Initial condition: $t=0$, $C_A=0$.

5. Rate of formation of gas product

Models 1 and 2:

$$r_G = \frac{dC_G}{dt} = K_G C_V^g \quad (4.8)$$

Initial condition: $t=0$, $C_G=0$.

6. Rate of formation of coke

Model 1:

$$r_C = \frac{dC_C}{dt} = K_C C_V^c \quad (4.9)$$

Model 2:

$$r_c = \frac{dC_c}{dt} = K_{C_1} C_{NV}^{C_1} + K_{C_2} C_V^{C_2} \quad (4.10)$$

Initial condition: $t=0$, $C_c=0$.

7. Rate of formation of residue

Model 1:

$$r_R = \frac{dC_R}{dt} = K_R C_{NV}^r \quad (4.11)$$

Model 2:

$$r_R = \frac{dC_R}{dt} = K_{R_1} C_{NV}^{r_1} + K_{R_2} C_V^{r_2} \quad (4.12)$$

Initial condition: $t=0$, $C_R=0$.

8. Rate of formation of hydrocarbons

Model 1 and 2:

$$r_H = \frac{dC_H}{dt} = K_H C_H^h \quad (4.13)$$

Initial condition: $t=0$, $C_H=0$.

4.5.2 Product Prediction Models

The catalytic conversion of the wood-oil was carried out in a fixed bed micro-reactor. Since conversions were high, the integral design equation 4.14 was used.

$$\frac{W}{F} = \int_{x_i}^{x_o} \frac{dx}{(-r_i)} \quad (4.14)$$

Substitution of the rate of formation of each product gave the equations needed for prediction of the conversions of each product, from which the yields were calculated. The product prediction models were

1. Organic distillate, D

Models 1 and 2:

$$\frac{W}{F} = \int_0^{x_o} \frac{dx}{(K_D C_V^d)} \quad (4.15)$$

2. Aqueous fraction, A:

Models 1 and 2:

$$\frac{W}{F} = \int_0^{x_o} \frac{dx}{(K_A C_V^a)} \quad (4.16)$$

3. Gas, G

Models 1 and 2:

$$\frac{W}{F} = \int_0^{x_o} \frac{dx}{(K_G C_V^g)} \quad (4.17)$$

4. Coke, C

Model 1:

$$\frac{W}{F} = \int_0^{x_0} \frac{dx}{(K_C C_V^c)} \quad (4.18)$$

Model 2:

$$\frac{W}{F} = \int_0^{x_0} \frac{dx}{(K_{C_1} C_{NV}^{c_1} + K_{C_2} C_V^{c_2})} \quad (4.19)$$

5. Hydrocarbons, H

Models 1 and 2:

$$\frac{W}{F} = \int_0^{x_0} \frac{dx}{(K_H C_V^h)} \quad (4.20)$$

6. Residue, R

Model 1:

$$\frac{W}{F} = \int_0^{x_0} \frac{dx}{(K_R C_V^r)} \quad (4.21)$$

Model 2:

$$\frac{W}{F} = \int_0^{x_0} \frac{dx}{(K_{R_1} C_{NV}^{r_1} + K_{R_2} C_V^{r_2})} \quad (4.22)$$

As can be seen, the product prediction equations depend on either the concentration of volatiles, C_V and/or non-

volatiles, C_{NV} which in turn depend on the kinetic parameters, i.e., reaction orders and rate constants. The solution procedure therefore required estimates of the values for the kinetic parameters as a first step. Having estimated the values for the kinetic parameters, equations 4.2 and 4.4 on one hand and 4.3 and 4.5 on the other were solved simultaneously for C_V and C_{NV} at each temperature and then substituted into the product prediction equations. Equations 4.2 and 4.4, and 4.3 and 4.5 forms a system of first order non-linear differential equations which can only be solved numerically. A program (Appendix E.1) which applies Runge-Kutta-Verner fifth order solution procedure using the subroutine IVPRK from the IMSL Math/Library [1992] was used. Following this the model equations were integrated to obtain the yields of each product. Again the program in Appendix E.1 was used to integrate the equations.

4.5.3 Kinetic Parameter Estimation

Step 1 and 2 (Both models)

Data for evaluating the kinetic parameters for these steps were obtained by calculating the concentrations of volatile and non-volatile fractions obtained at each temperature from the vacuum distillation of the wood-oil at 172 Pa. The calculations were based on the assumption that the intermediate volatile and non-volatile products obtained from the vacuum distillation have the same composition as that

obtained during the processing of the wood-oil in the fixed bed reactor at atmospheric pressure. Also, it was assumed that the reaction of wood-oil into these intermediate fractions followed first order kinetics and that the distillation temperatures can be correlated directly to similar values at atmospheric pressure. The concentrations were fitted to the following relations

$$C_{NV} = K_{NV} C_W = K_{o1} e^{-E_1/RT} C_W \quad (4.23)$$

$$C_V = K_V C_W = K_{o2} e^{-E_2/RT} C_W \quad (4.24)$$

Steps 3-8 (model I) and 3-10 (model II)

It was assumed in this work that each path involved elementary reactions, so that the rate constant dependence on temperature followed the Arrhenius equation. Following this the rate of formation of each product was fitted to the power law rate model

$$r_i = K_i C_i^{a_i} = K_{oi} e^{-\frac{E_i}{RT}} C_i^{a_i} \quad (4.25)$$

This led to the estimation procedure which required determining values of the kinetic parameters, K_i , E_i and a_i for each path of the reaction network. It consisted of obtaining rate-concentration data for each path as a first

step, followed by the application of equation 4.25 in a non-linear least square regression program (Appendix E.2) to estimate the parameter values.

Rate-concentration data was obtained by carrying out a series of kinetic runs using the non-volatile and volatile components of the wood oil (as feeds) separately. This was carried out using different inlet concentrations at fixed flow rate and mass of catalyst. The rates were then calculated by application of equation 2.11 and the parameters estimated by equation 4.25. Rate-concentration data used in the parameter estimation for steps 3 and 4 (model 1) and steps 3-5 (Model 2) were obtained by upgrading of the non-volatile fraction and for steps 5-8 (model 1) and steps 6-10 (model 2) by upgrading the volatile fraction of the wood-oil.

4.5.4 Rates of Formation of Products

The rates of formation of the products based upon experimental runs are presented in Appendix F.2. As can be seen, the values of the rates were affected by the temperature and concentration. However, the rates increased with temperature and decreased with concentration for aqueous fraction, coke and gas. The rates for organic distillate, hydrocarbon and residue decreased with temperature and increased when the feed concentration was lowered. The highest rates were recorded for the organic distillate and its hydrocarbon fraction. The lowest rates were the residue and

water formation reactions. The rates of formation of the products followed the general order: organic distillate > hydrocarbons > residue > coke > gas > aqueous fraction.

4.5.5 Reaction Rate Constants

Reaction rate constants are an indication of the speed of formation of each product [Levenspiel, 1972; Rase, 1977; Fogler, 1989]. The rate constants (Appendix F.2) ranged from 10^{-6} (aqueous fraction formation) to 1.81 (volatile formation) implying that the fastest step was about 6 orders of magnitude faster than the slowest step. The aqueous formation step being the slowest step implied that dehydration was a difficult reaction step in the upgrading of wood-oil. The ease of formation of each product based on the rate constants followed the general order: organic distillate > hydrocarbons > gas > residue, coke > aqueous fraction.

4.5.6 Activation Energies

A wide range of activation energies ranging between 10^2 to 10^4 Kcal/Kmol were obtained (Appendix F.2). The activation energies were calculated on the assumption that each reaction step or path could be assumed elementary so that the Arrhenius equation could be applied. It is known that the magnitude of the activation energy is an indication of how much energy is required (endothermic process) or needs to be released (exothermic process) to cause the reaction to occur. It also

reflects on the sensitivity of the reaction to temperature. Again, the highest activation energy was for the aqueous fraction formation (most temperature sensitive) and the lowest, the organic distillate (least temperature sensitive) formation.

4.5.7 Reaction Orders

The reaction orders (Appendix F.2) ranged between 0.7 (gas formation) and 2.5 (Residue formation). The fractional reaction orders implied complexity of the conversion process [Swinboure, 1971; Espenson, 1981]. All the orders were positive which implies that higher feed concentrations do not generally inhibit or slow the conversion process. Also, temperature did not have much influence on the order of reaction. The only exception to this was the residue formation step which showed an increase in reaction order with increase in temperature. This increase may imply that higher concentrations of non-volatile fraction do favour the rates of formation of the residue fraction.

4.5.8 Experimental Versus Model Prediction of Yields of Products

The experimental results on the upgrading of the wood-oil to hydrocarbon-rich fraction in section 4.3 and the model prediction of experimental values are compared and discussed in this section. Discrimination between the two models was

made by comparing their trends, predicted values of the products as well as applying the criterion that values of sum of squares of the divergence from experimental results, D-parameter [Froment and Bischoff, 1979], should be minimum for the best model. The D-parameter is defined over the temperature range covered by the relation

$$D_i = \sum (y_i^p - y_i^{\text{exp}})^2 \quad (4.26)$$

Organic Distillate and Hydrocarbon Fraction

It has already been mentioned that the major purpose of the mathematical modeling was to derive models that could provide estimates of the organic distillate and its hydrocarbon content given any wood-oil with known composition. The experimental versus model predictions are shown in Figures 4.37 and 4.38. As can be seen, both models predicted with reasonable accuracy the trends and values of the experimental results over the entire temperature range. From values of the D-parameter, model II was a better model than model I.

Aqueous Fraction

Figure 4.39 shows the experimental and model predictions of the aqueous fraction formed at each temperature. As can be seen, model II predicted the aqueous fraction formation trend more accurately than model I. It can also be seen that model

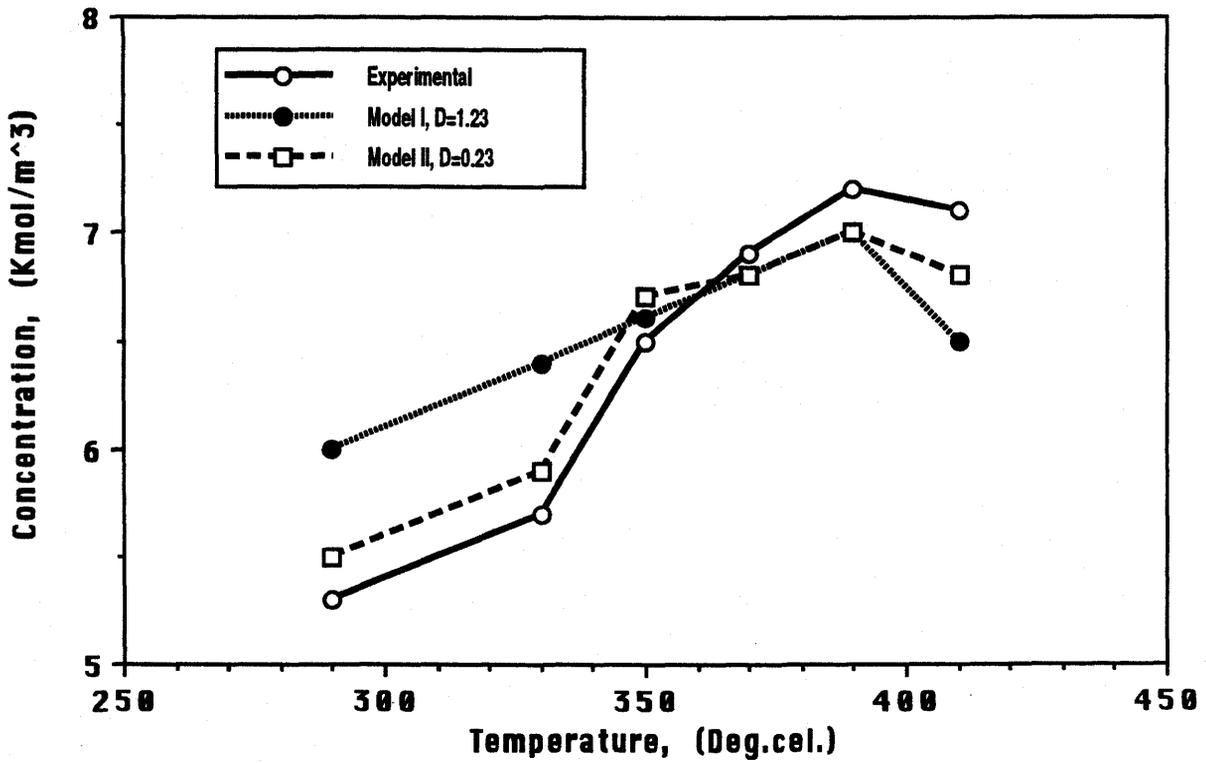


Figure 4.37 Experimental versus model prediction of organic distillate.

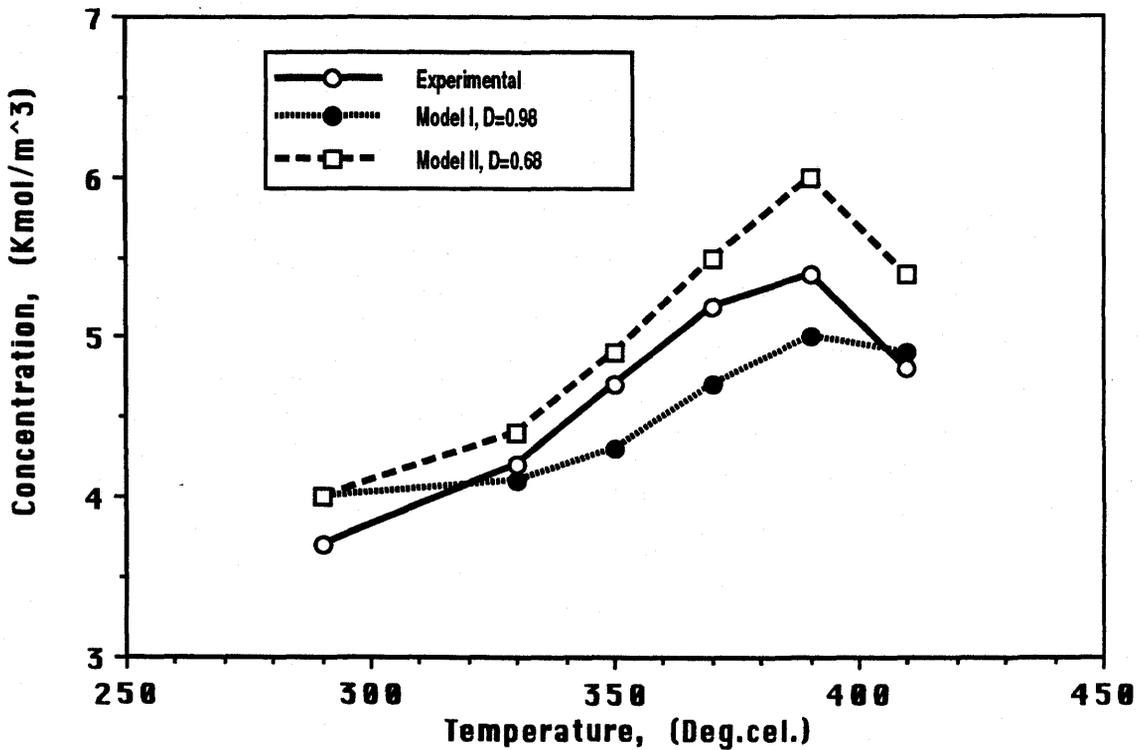


Figure 4.38 Experimental versus model prediction of hydrocarbons.

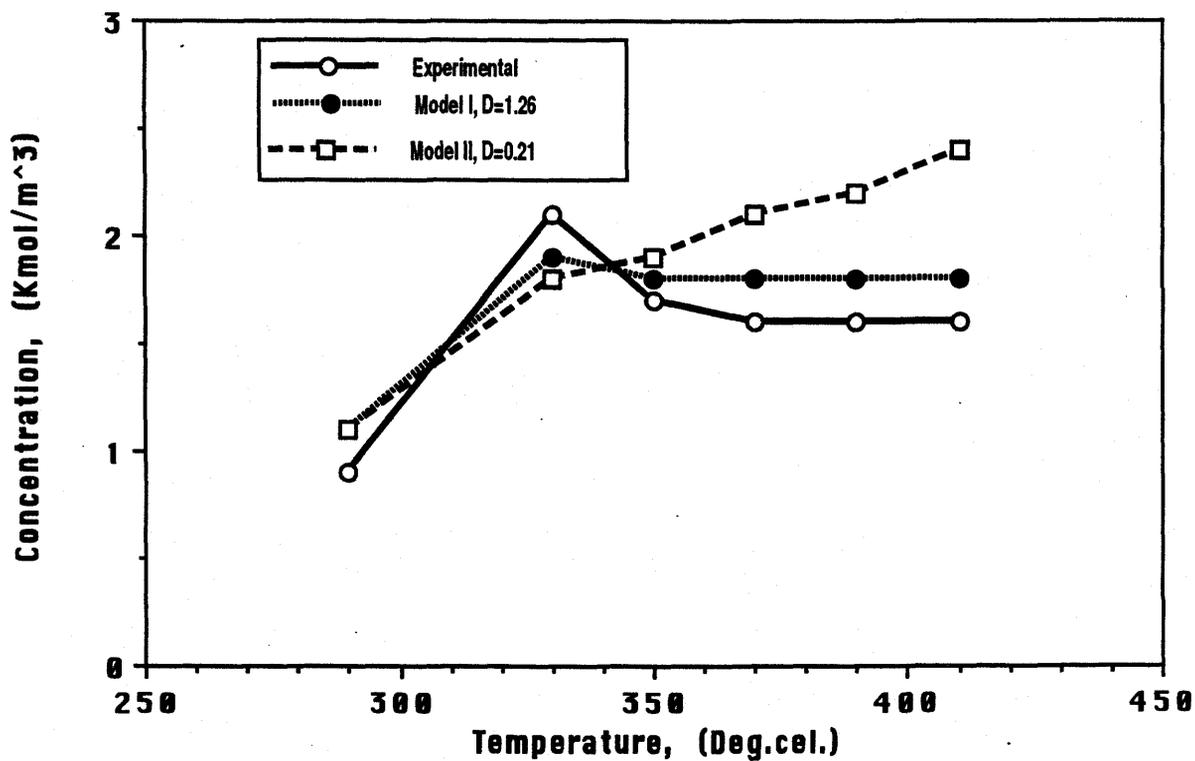


Figure 4.39 Experimental versus model prediction of aqueous fraction.

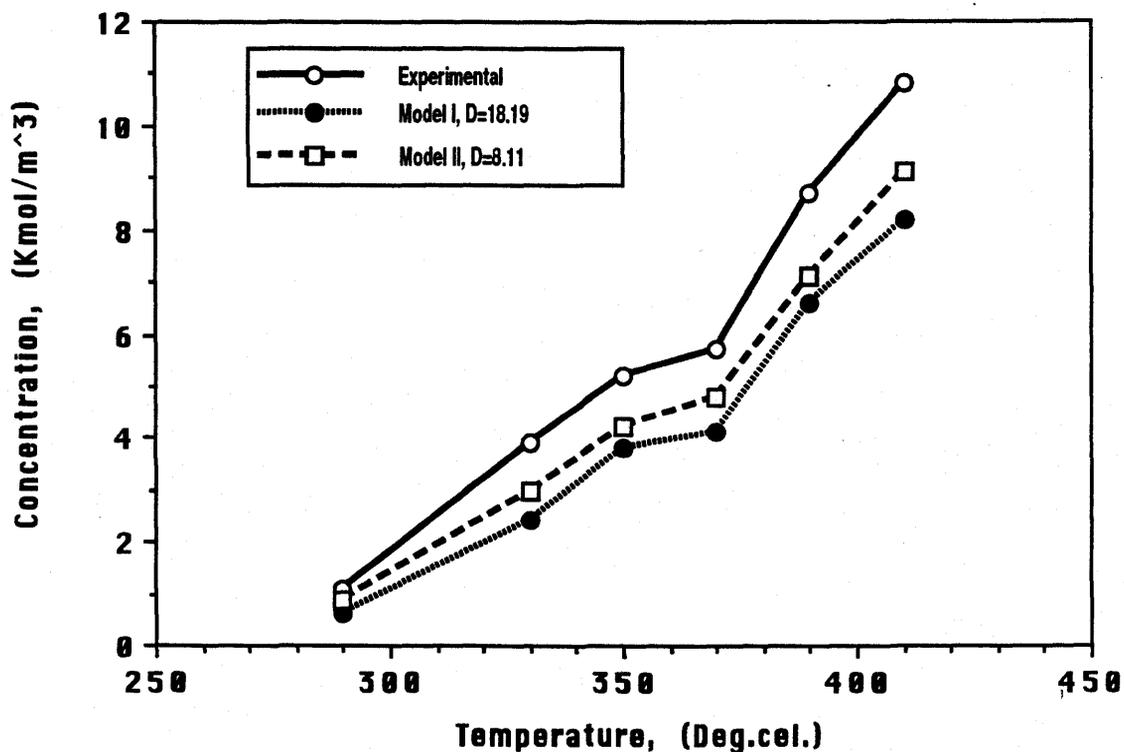


Figure 4.40 Experimental versus model prediction of coke formation.

I diverged after 330 °C, that is, it predicted an increasing dehydration instead of reaching a maximum at that temperature. Comparing the two models by the D-parameter shows that divergence of model II was minimal and as a result is the better model in predicting the aqueous fraction formation.

Coke Formation

Both models predicted the trend of coke formation very accurately as shown by their monotonic increase with temperature in Figure 4.40. Values obtained from model II was closer than model I, probably because model II was derived based on coke formation from reactions of both volatile and non-volatile components, whereas model I was derived on the assumption that coke formation was predominantly from the reactions of the volatile components alone. The model compound reactions and also the reactions involving the non-volatile alone over HZSM-5 also supported the formation of coke from both volatile and non-volatile components. A D-parameter of 8.11 from model II compared to 18.19 by model I shows that model II has the least deviation from experimental values and therefore is the superior model.

Gas Formation

Figure 4.41 shows the experimental versus model prediction of gas formation. Both models predicted the trend of gas formation with temperature rather accurately. However,

they overestimate the experimental results. This discrepancy may be because it was assumed that gas formation from the cracking of non-volatile components was negligible compared to that from the volatile components. Again model II provided a closer prediction of the experimental results compared to model I.

Residue formation

Figure 4.42 shows the experimental and model predictions of the residue fraction. As can be seen, the trends are fairly similar beyond 330 °C. Below this temperature, the model values deviate exceedingly from the experimental values. However, as can be seen from the D-parameter values, these deviations are very small compared to the deviations from the coke formation models. Model II proved to be the better model and this can again be explained from the point that derivation of model II was based on the combined formation of residue from both volatile and non-volatile components compared to model I which was based on residue formation from the reactions of non-volatile alone. Experimental observations from the model compound reactions have shown that condensation reactions of volatile ethers and phenols could lead to the formation of non-volatile (residue) molecules.

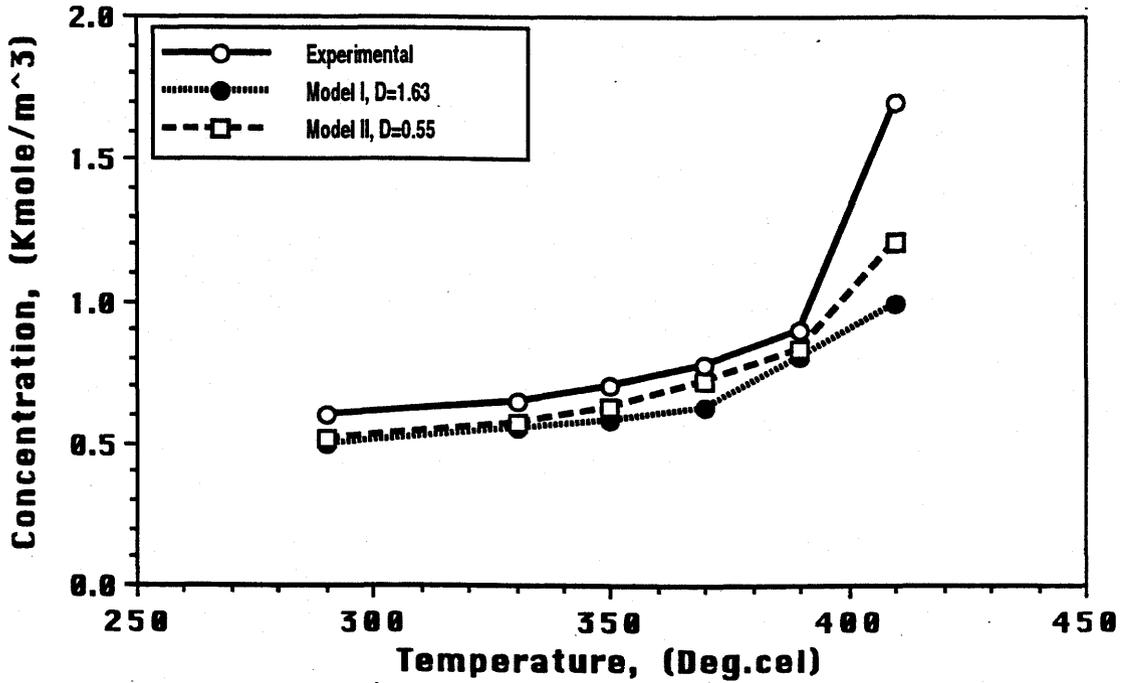


Figure 4.41 Experimental versus model prediction of gas formation.

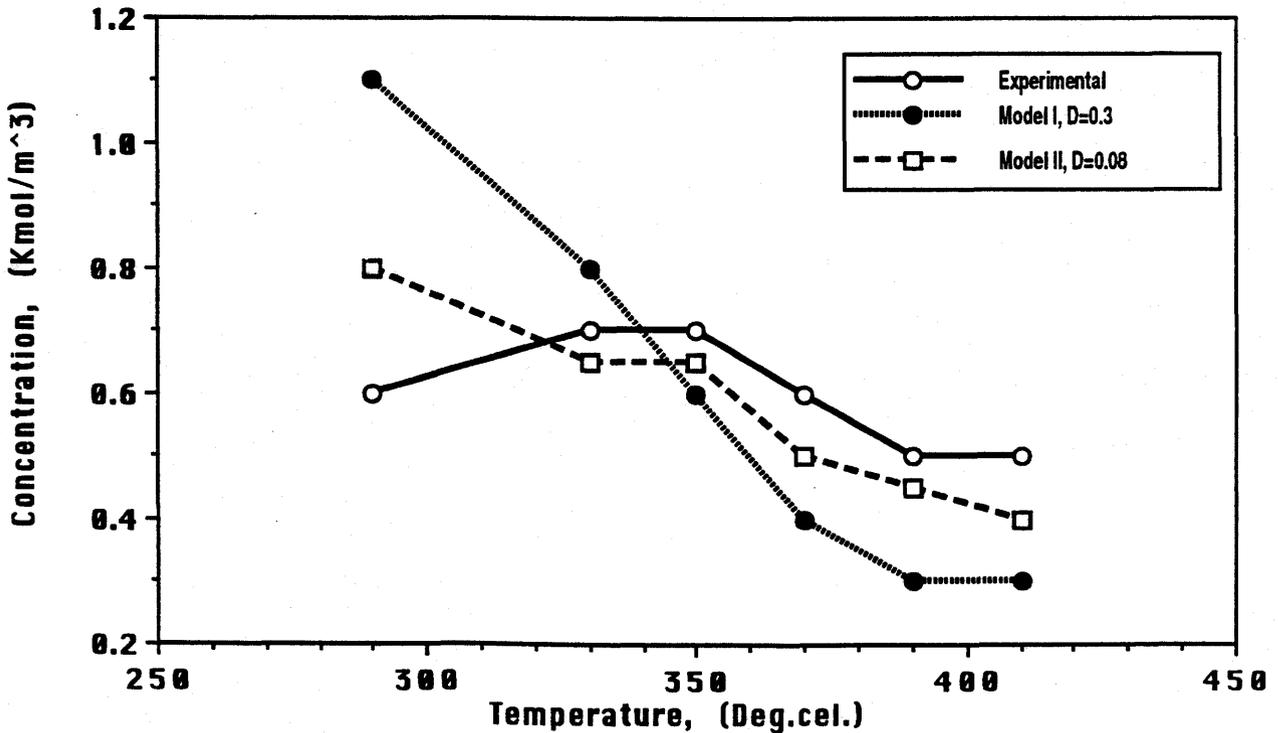


Figure 4.42 Experimental versus model prediction of residue formation.

4.5.9 Model Assessment and Improvement

For each product it has been shown that model II which accounted for coke and residue formation from reactions of both volatile and non-volatile components was the superior model. From these results it can also be concluded that reaction pathway II (Figure 4.36) better explained the paths through which wood-oil was converted than pathway I (Figure 4.35). The major products of interest, ie., organic distillate and its hydrocarbon content were estimated reasonably accurately by model II. It has also been shown that the power law assumption of the rate model works well. The model was easy to use and simple considering the complexity of the conversion reaction. However, this could be improved by application of LHHW rate models which could provide vital information on adsorption and further insight into the reactions.

4.5.10 Hydrocarbon Selectivity

The composition of a reaction mixture for complex feeds can be described by either the conversion, yield or selectivity parameter [Hill, 1977; Wojciechowski and Corma, 1986]. Due to its complexity, calculation of the conversions for wood-oils is usually complicated. On the other hand, the yields and selectivities of the desired products are simpler and usually straight forward calculations are possible. Also, the selectivity relations have a number of advantages in that

unlike conversion, it can be manipulated in various ways to optimize the yield of the desired product and minimize the undesired ones. In most industrial situations, reactor designers have opted for selectivity even though it often led to low activity [Hill, 1977]. For gas oil cracking, models that predict gasoline selectivity have been shown to be especially more important than those that predict only the conversion [Wojciechowski, 1988]. Knowledge of the selectivity relations can also aid in the selection of reactors and development of efficient reaction conditions.

In this work the desired products were hydrocarbons, so that the selectivity was defined with respect to the hydrocarbon fraction. The undesired products were aqueous fraction, coke, gas and residue. The coke and residue fractions were the most worthless products. On the other hand, it was desired to achieve high deoxygenation, so that the formation of water and carbon oxides are not in themselves undesired products as such. As a result, selectivities for hydrocarbons were defined based on the coke and residue fractions.

Selectivity has been defined as

$$S_H = \frac{I_D}{I_U} \quad (4.27)$$

On insertion of the rate equations, the hydrocarbon selectivity can be defined based on either coke or residue or

combined coke and residue by following relations

$$S_{H/C} = \frac{I_H}{I_C} = \frac{K_H C_V^h}{K_{C_2} C_V^{C_2} + K_{C_1} C_{NV}^{C_1}} \quad (4.28)$$

$$S_{H/R} = \frac{I_H}{I_R} = \frac{K_H C_V^h}{K_{R_2} C_V^{R_2} + K_{R_1} C_{NV}^{R_1}} \quad (4.29)$$

$$S_{H/R} = \frac{I_H}{I_R + I_C} = \frac{K_H C_V^h}{K_{R_2} C_V^{R_2} + K_{R_1} C_{NV}^{R_1} + K_{C_2} C_V^{C_2} + K_{C_1} C_{NV}^{C_1}} \quad (4.30)$$

Plots of the hydrocarbon selectivity with temperature and concentration based on coke as the undesired product are shown in Figure 4.43. As can be seen, higher selectivities are favoured at low concentrations and low temperatures. On the other hand, the selectivity based on undesired residue shows that higher values are obtained at lower concentrations and higher temperatures (Figure 4.44). These results show that if the objective was coke reduction, then processing at lower temperatures would be desired. However, if residue reduction was the main objective, then processing at higher temperatures was best. In wood-oil processing it is desired that coke and residue formation are kept to a minimum simultaneously. Hence, it was essential to evaluate the selectivity based on combined coke and residue formation.

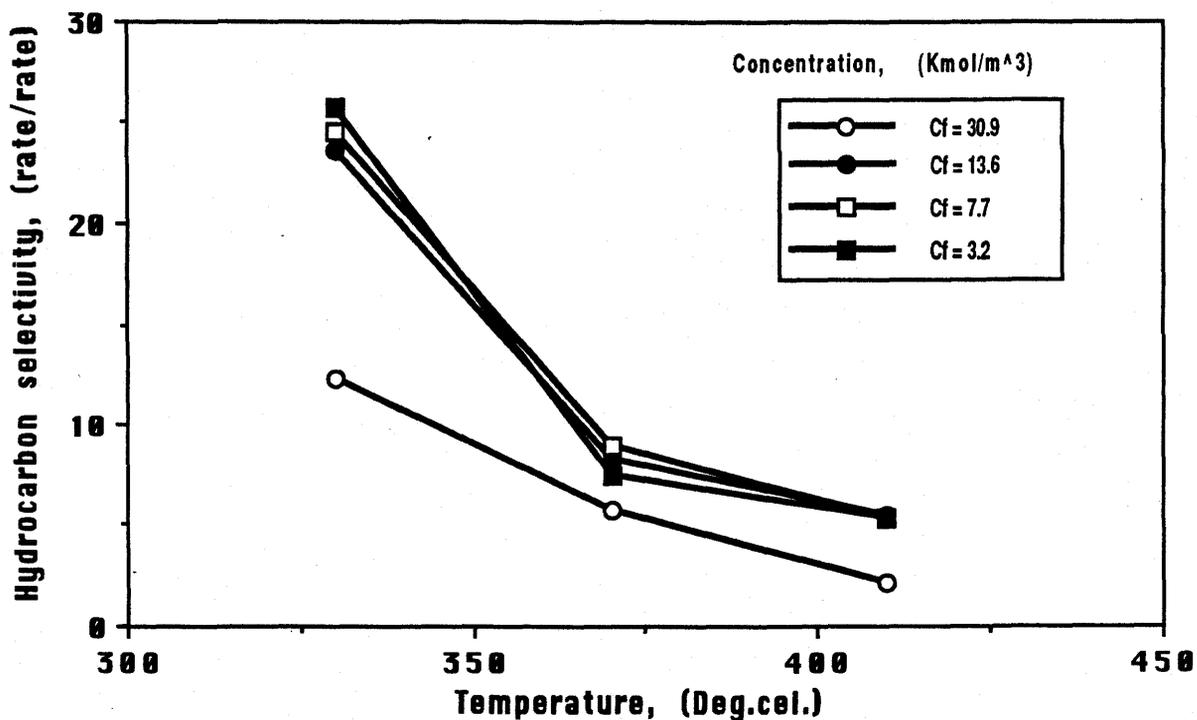


Figure 4.43 Hydrocarbon selectivity based on coke as undesired product.

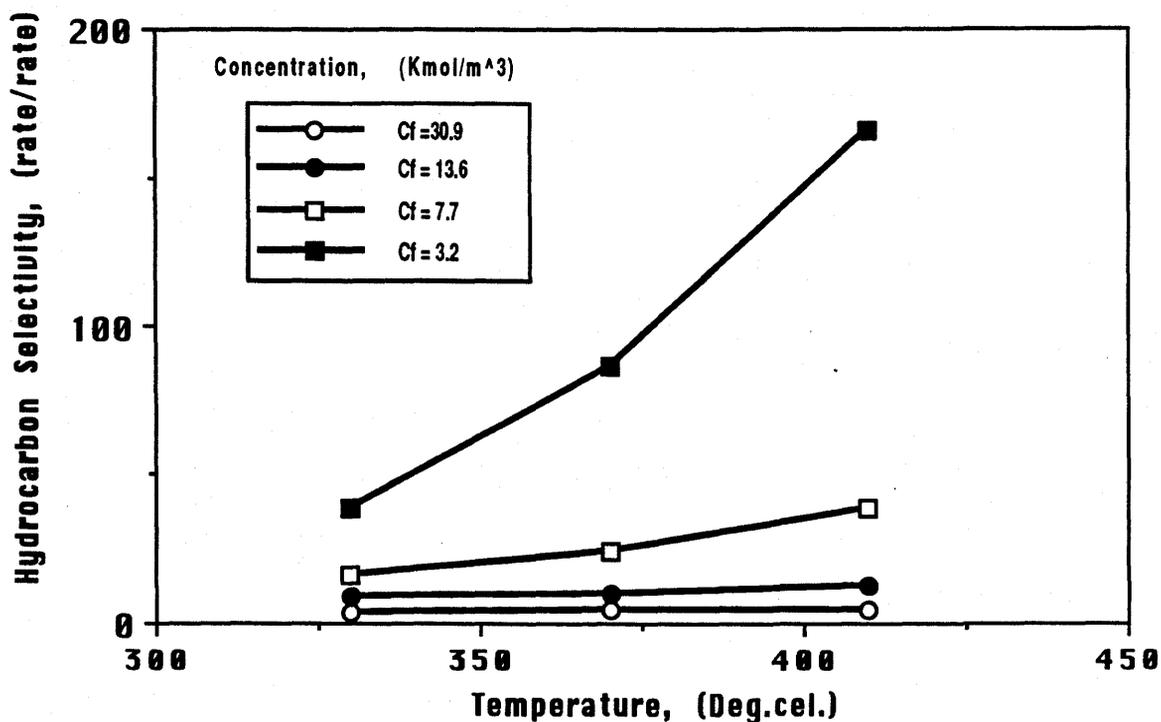


Figure 4.44 Hydrocarbons selectivity based on residue as undesired product.

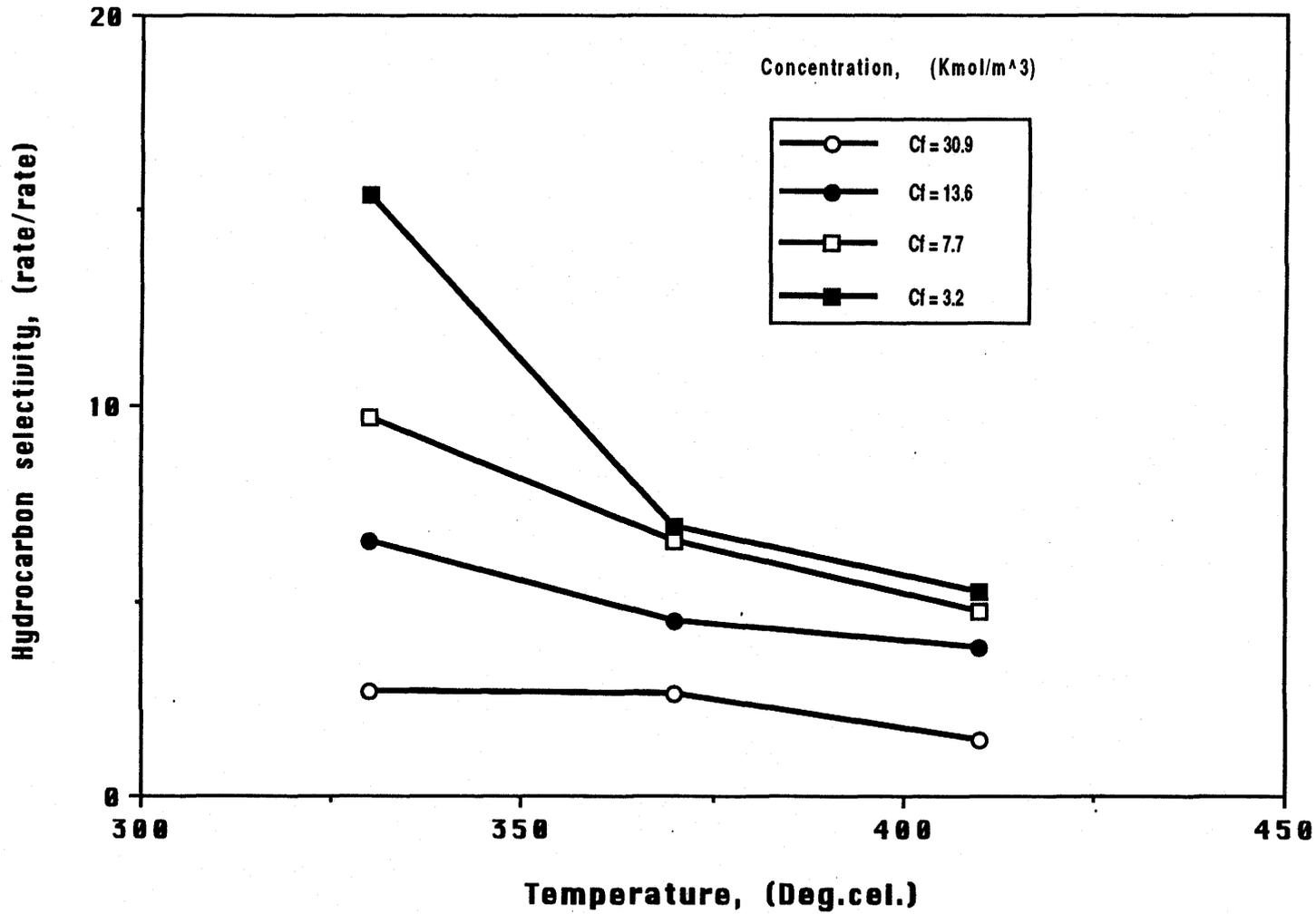


Figure 4.45 Hydrocarbon selectivity based on combined residue and coke as undesired products.

The selectivity based on combined coke and residue fractions are plotted in Figure 4.45. The combined effect shows that lower temperatures and concentrations are best for achieving higher selectivities for hydrocarbons. However, the problem with these operating conditions is that processing at low temperatures and concentrations results in low conversions and smaller yields of hydrocarbons. Also, lower temperatures are characterised by high fractions of unreacted feed or tars which the parameter does not account for.

As shown by the selectivity relations, there are a number of ways by which the hydrocarbon selectivity could be improved. The first is reducing the rate of formation of the coke forming step by manipulation of the kinetic parameters. This rate appears in the denominator of the selectivity relations. In wood oil processing, a number of processing conditions can be utilized to reduce coke formation without lowering the reaction temperature. This has been carried out by either raising the hydrogen-to-carbon ratio of the feed before upgrading or co-feeding with steam. These two practises have been employed in section 4.3. A second approach is to reduce the residue forming step. Employing conditions that would improve the cracking of non-volatile fraction without employing excessive temperatures or very low feed concentrations is the most likely possibility. This can be carried out by using a more efficient cracking catalyst or increasing the acidity of the zeolite catalysts.

It has been shown that selectivity relations could be derived and used to identify the conditions for achieving higher selectivity for hydrocarbons. However, this is at the expense of higher conversion to hydrocarbons.

5. CONCLUSIONS

1. Preparation, Characterization and Stability Analysis of Wood-oil.

a. The wood-oil, produced from the HPL of aspen poplar wood, was a complex mixture of acids, esters, alcohols, aldehydes, aromatic and aliphatic hydrocarbons, furans, ethers and phenols.

b. A maximum amount (62.3 wt%) of organic liquid (distillate) product was obtained from wood-oil by fractionation at 200 °C and 172 Pa.

c. The wood-oil was unstable and its viscosity and chemical composition changed with time, probably due to polymerization or the oxidative coupling of some of the wood-oil components.

d. The stability of the wood-oil improved in the presence of tetralin. This was explained on the basis of a free radical mechanism and the hydrogen-donor properties of tetralin.

2. Upgrading of Wood-oil in the Presence and Absence of Steam

a. The wood-oil was catalytically upgraded using HZSM-5 to yield a highly aromatic liquid product (maximum 58.3 wt% at 390 °C in the absence of steam and 65.0 wt% at 370 °C in the presence of steam). It was rich in benzene, toluene, xylenes,

other alkylated benzenes in the gasoline boiling point range, phenol and alkylated phenols. The yield and selectivity of these compounds were strong functions of the temperature and process time.

b. Upgrading in the presence of steam resulted in higher organic distillate (4 to 18 % increase) and lower coke formation (40 to 60% decrease) compared to the operation without steam. However, lower yields and selectivities for hydrocarbons were obtained in the presence of steam.

c. HZSM-5 could be regenerated easily and re-used with little change in its performance.

d. Upgrading the volatile portion (62.3 wt%) of the wood-oil separately from the non-volatiles (37.7 wt%) resulted in 72.5 to 92.3 wt% organic distillate yields which contained between 51.2 to 72.7 wt% hydrocarbons. This shows that higher hydrocarbon yields can be obtained from processing the wood-oil volatiles.

3. Conversion and Performance of Various Catalysts in Upgrading the Wood-oil

a. The wood-oil was converted over different zeolite and amorphous silica-alumina catalysts to organic distillate products rich in various concentrations of hydrocarbons. Maximum hydrocarbon yields and selectivities were 22.1 wt% and 0.29 for silicalite, 27.5 wt% and 0.28 for H-mordenite, 21.0

wt% and 0.25 for H-Y, and 26.2 wt% and 0.36 for silica-alumina compared to 42.1 wt% and 0.78 for HZSM-5. The yields and selectivities for HZSM-5 and silicalite were mostly for gasoline range hydrocarbons and for H-mordenite and H-Y they were for kerosene range hydrocarbons. The hydrocarbon fraction from silica-alumina did not produce any defined distribution.

b. The relative performance of the catalyst was rated as follows:

i. Based on yield of hydrocarbons

HZSM-5> H-mordenite> H-Y> Silicalite, Silica-alumina.

ii. Based on selectivity for hydrocarbons

HZSM-5> Silicalite, H-mordenite> H-Y> Silica-alumina.

iii. Based on effectiveness of deoxygenation

HZSM-5> Silica-alumina> H-Y>Silicalite, H-mordenite.

iv. Based on conversion of non-volatile fraction

Silica-alumina> HZSM-5> H-mordenite> Silicalite> H-Y.

v. Based on coke formation

Silicalite> HZSM-5> H-mordenite> Silica-alumina> H-Y.

c. The catalyst shape selectivity, acidity and pore size affected the cracking and deoxygenation of the wood-oil as well as the yield, selectivity and distribution of hydrocarbons.

4. Kinetic Modeling I: Model Compound Studies and Reaction Pathways

a. Reactions of model compounds provided useful information on the chemical steps through which the various chemical groups reacted over HZSM-5 catalyst. With this information it was possible to propose two rival reaction pathways for the conversion of the wood oil to various products.

b. The model compound studies showed that phenols and ethers react to relatively lower extents compared to acids, alcohols, esters, aldehydes and ketones. The major portion of the hydrocarbons produced, especially aromatic hydrocarbons, were predominantly the reactions of acids, alcohols, esters, aldehydes and ketones. Coke formation could be closely linked with reactions of acids, alcohols, esters and aldehydes and ketones and residue formation, with reactions of phenols and ethers.

c. To obtain the hydrocarbon-rich product from the processing of the wood-oil, three groups of reactions must occur. The first group of reactions are the primary reactions including cracking and deoxygenation. Secondary cracking, oligomerization, olefin formation, hydrogen transfer and cyclization make up the secondary or intermediate reaction group. The third group of reactions are the terminal or terminating reactions. This includes alkylation, isomerization, disproportionation and polymerization

reactions.

5. Kinetic Modeling II: Chemical Kinetics, Parameter Estimation and Model Derivation and Prediction

a. On the assumption that rate of each path could be described by the power law rate model, it was possible to obtain estimates of the values of the kinetic parameters, i.e., activation energies, rate constants and reaction orders. Also, using the integral reactor design equation, product prediction models were derived that gave reasonably accurate results for the yields of products obtained from the conversion of the wood-oil over HZSM-5. Model discrimination based on predicting the trends and values (yields) of the products as well as on D-parameter aided in selecting the model and the reaction pathway that best described the conversion of the wood-oil.

b. The values of the kinetic parameters, have shown that the upgrading of the wood-oil to reaction products proceeds through a complex mixture of reactions.

c. By deriving a hydrocarbon selectivity relation it was shown that lower temperatures and concentrations favoured the selectivity of hydrocarbons. However, this was at the expense of achieving higher yields of hydrocarbons.

6. RECOMMENDATIONS

1. Under similar reaction conditions, coke formation has been mentioned to be higher in fixed bed compared to fluidized bed operations. For this reason it is recommended that a fluidized bed reactor be used if reduction in coke formation was required.

2. Due to the temperature sensitivity, tar and char formation pose serious problems during the upgrading wood-oils. Although in this work this was reduced by co-processing with tetralin, a two-temperature stage reactor is recommended for further reduction in the tar and char formation. The first temperature stage, operating at a low temperature will serve to stabilize the wood-oil components before reaction in the second stage.

3. The activity of zeolite catalysts has been mentioned to be directly proportional to its acidity. Also, cracking and aromatization reactions which are essential for hydrocarbon formation are known to be enhanced by acid sites. Since the acidity of the catalyst used in this work was fixed, it is recommended that zeolites with higher catalyst acidity should be used. Using galuminate in place of aluminate in HZSM-5 preparation is recommended.

Also, a dual function catalyst that combines the shape selectivity of zeolites with the hydrogenating function of a

metal catalyst can also be used to enhance deoxygenation while improving upon the H/C ratio.

4. In this work no attempts were made to separate or isolate the very important chemicals such as benzene, toluene, xylenes and phenols. Since these compounds find very important applications in the chemical industries, it is recommended that methods should be adopted whereby these chemicals could be separated from the organic distillate product.

5. It is also recommended that the tetralin used for upgrading should be separated from the organic distillate. This could be rehydrogenated and reused. On the other hand, portions of the organic distillate could also be recycled by mixing with fresh feed and upgraded. By so doing, hydrogen-donor costs could be substantially reduced.

7.

REFERENCES

1. Antal, M.J. Jr., "Biomass pyrolysis: a review of the literature, Part II- Lignocellulose Pyrolysis", in Advances in Solar Energy, 2, K.W. Boer, and J.W. Duffie (eds.), American Solar Energy and Plenum Press, New York, 175-255, (1985).
2. Appell, H.R., "The production of oil from wood waste, in Fuels from Wastes, L.L. Anderson and D.A. Tillman (eds.), 121-140, (1977).
3. Araya, P.E., S.E. Droguett, H.J. Neuburg and R. Badilla-Ohlbaum, "Catalytic wood liquefaction using a hydrogen donor solvent", *Can. J. Chem. Eng.*, 64, 775-780, (1986).
4. Auld, D.L., C.L. Peterson, and R.A. Korus, "Production, processing and utilization of rapeseed oil as a diesel fuel substitute, in Energy from Biomass and Wastes XII, D.L. Klass, (ed.), *Inst. Gas Tech.*, Chicago, 1141-1151, (1989).
5. Ayres, W.A., "Commercial application of oxygenated oil derived from an entrained flow ablative fast pyrolysis system, in, Energy from Biomass and Wastes XII, Klass, D.L., (Eds.), *Inst. Gas. Tech.*, Chicago, Il., 1141-1151, (1989).
6. Baker, E.G and D.D. Elliot, "Catalytic hydrotreating of biomass-derived oils", Paper presented at conference on Production, Analysis and Upgrading Of Oils From Biomass, ACS., Denver, 257, (1987).
7. Beckman, D. and A. Oestman, "Upgrading of biomass-derived oils", *Can. Chem. News*, 31, 15-18, (1985).
8. Bockrath, B.C., "Chemistry of hydrogen-donor solvents", in *Coal Science*, M.L. Gorbaty, J.W. Larsen and I. Wender (eds.) Academic Press, New York, 2, 65-120, (1983).
9. Boocock, D.G.B., D. Mackay, H. Franco, and P. Lee, "The production of synthetic organic liquids from wood using a modified nickel catalyst", *Can. J. Chem. Eng.*, 58, 466-469, (1980).
10. Boocock, D.G.B., F. Agblevor, A. Chowdhury, M. Holysh, and F. Porretta, "The liquefaction of poplar by rapid aqueous pyrolysis: Results from semi-continuous and batch units", in Fifth Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 450-454, (1984).
11. Boocock, D.G.B., F. Agblevor, S. Allen, A. Chowdhury, and L. Kosiak, "Wood liquefaction by steam treatment", in Sixth Canadian Bioenergy R&D Seminar, C. Granger (ed.), 471-475, (1987).

12. Boocock, D.G.B., A. Chowdhury, S.A. Allen, and R.D. Hayes, "The production and evaluation of oils from the steam pyrolysis of poplar chips", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symp. Ser., 32, 90-97, (1987).
13. Boocock, D.G.B., S.G. Allen, A. Chowdhury and R. Fruchtl, "Producing, evaluating and upgrading oils from steam liquefaction of poplar chips", in Production, Analysis and Upgrading of Oils from Biomass, ACS Symp. Ser., 92-103, (1988).
14. Boocock, D.G.B., A. Chowdhury, L. Kosiak and R.A. Fruchtl, "The steam/water liquefaction of polar wood in a gravity fed reactor: a) The effect of feed size and b) Upgrading of wood oil model compounds", Proceedings of Seventh Canadian Bioenergy R&D Seminar, Ottawa, Ontario, 693-696, (1989).
15. Bungay, H.R. and R.F. Ward, "Fuels and chemicals from crops", in Fuels from Wastes, L.L. Anderson, L.L. and D.A. Tillman (eds.), 105-120, (1977).
16. Breck, D.W., Zeolite Molecular Sieves: Structure, Chemistry and Use, Robert Krieger Publishing Company, Florida, 120-124, 231, 253, 1984.
17. Campbell, I., "Principles of reactions on solid catalysts", in Biomass, Catalysts and Liquid Fuels, Holt, Rinehart and Winston, 106-121, 1983.
18. Carberry, J.J., "Analyses and design of heterogeneous reactors", in Chemical and Catalytic Reaction Engineering, McGraw-Hill Book Company, 519-526, 1976.
19. Chang, C.D. and A.J. Silvestri, "The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts", J. Catal., 47, 249-259, (1977).
20. Chang, C.D., W.H. Lang, and R.L. Smith, "The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts II. Pressure effects", J. Catal., 56, 169-173, (1979).
21. Chang, C.D., Hydrocarbons from Methanol, Marcel Dekker, New York, 7-37, 1983.
22. Chantal, P.D., S. Kaliaguine, K.L. Grandmaison and A. Mahay, "Production of hydrocarbons from aspen poplar pyrolytic oils over HZSM-5", App. Catal., 10, 317-332, (1984).
23. Chantal, P.D., S. Kaliaguine, and J.L. Grandmaison,

- "Reactions of phenolic compounds over HZSM-5", *Appl. Catal.*, 18, 133-145, (1985).
24. Chen, N.Y., J.N. Miale, and W.J. Reagan, U.S. Pat. 4 112 056, (1973).
25. Chen, N.Y. and T.Y. Yan, "M2-forming: A process for aromatization of light hydrocarbons", *Ind. Eng. Chem. Proc. Des. Dev.*, 25, 151-155, (1986).
26. Chen, N. Y., D.E. Walsh and L.R. Koenig, "Fluidized bed upgrading of wood pyrolysis liquids and related compounds", in Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series 376, Washington, DC 277-289, (1988).
27. Chen, N.Y., W.E. Garwood, and F.G. Dwyer, Shape Selective Catalysis in Industrial Applications, Marcel Dekker Inc., 65-146, 155-196, 1989.
28. Chornet, E., D. Eugene, D. and R.P. Overend, "Fluidodynamic effects in the fractional solubilization of biomass leading to liquefaction", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne and L.K. Mudge (eds.), 839-848, (1982).
29. Chornet, E. and R.P. Overend, "Biomass liquefaction: An overview", in Fundamentals of Thermochemical Conversion, R. P. Overend, T.A. Milne and L.K. Mudge (eds.), 967-1002, (1982).
30. Chum, H.L., J.W. Diebold, J.W. Scahill, D. Johnson, S. Black, H. Schoede and R.E. Kreibich, "Biomass pyrolysis oil feedstocks for phenolic resins", in Adhesives from Renewable Resources, R.W. Hemingway, A.H. Connor and S.J. Branham (eds.), ACS Symp. Ser., 385, Washington, 135-151, (1989).
31. Churin, E., P. Grange and B. Delmon, "Quality improvement of pyrolytic oils from biomass", in *Energy from Biomass*, 4, Proceedings of the third contractors meeting, G. Grassi, D. Purrnitz and H. Zibetta (eds.), 504-509, (1988).
32. Cooper, D., M. Douglas, O. Ali, S. Afrachtehfar, D. Ng, and N. Cooke, "A low-temperature process for the conversion of wood to liquid fuels and chemicals using hydrogen iodide", in Fifth Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 455-459, (1984).
33. Cusumano, J.A., R.A.D. Betta and R.B. Levy, *Inorganic Chemistry*, in Catalysis in Coal Conversion, Academic Press, 107-108, 1978.
34. Dao, L.H., P. Hebert, A. Houle and L. Jutras, "Direct

catalytic thermoconversion of biomass into liquid fuels and chemical feedstocks", in Fifth Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 460-464, (1984).

35. Dao, L.H., M. Haniff, A. Houle and D. Lamothe, "Reactions of model compounds of biomass-pyrolysis over ZSM-5 zeolite catalyst", in Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading, E.J. Soltes, and T.A. Milne, (eds.) 328-344, (1988).

36. Davis, H.G., M.A. Eames, C. Figueroa, R.R. Gansley, L.L. Schaleger and D.W. Watt, "The products of direct liquefaction of biomass", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne, and L.K. Mudge, (eds.), 1027-1032, (1982).

37. Decroocq, D., "The nature of the key operating variables or parameters and their effects on the performances of the reactor and regeneration", in Catalytic Cracking of Heavy Petroleum Fractions, Edition Technip, 37-72, 1984.

38. Diebold, J. and J. Scahill, "Production of primary pyrolysis oils in a vortex reactor", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series, 32, 21-28, (1987).

39. Diebold, J., and J. Scahill, "Biomass to gasoline (BTG): Upgrading pyrolytic vapours to aromatic gasoline with zeolite catalysts at atmospheric pressure", in Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series 376, 264-276, (1988).

40. Dyer, A., An Introduction to Zeolite Molecular Sieves, John Wiley & Sons, 22-54, 117-126, (1988).

41. Eager, R. L., J.F. Mathews and J.M. Pepper, "Studies on the products resulting from the conversion of aspen poplar to an oil", Can. J. Chem., 59, (14), 2191-2198, (1981).

42. Eager, R.L., J.F. Mathews and J.M. Pepper, "Liquefaction of aspen poplar wood", Can. J. Chem. Eng., 60, 289-294, (1982).

43. Eager, R.L., J.F. Mathews and J.M. Pepper, "Liquefaction of aspen poplar to produce an oil and chemicals", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne and L.K. Mudge (eds.), 1051-1071, (1982).

44. Eager, R.L., J.M. Pepper and J.F. Mathews, "A small scale semi-continuous reactor for the conversion of wood to fuel oil", Can. J. Chem. Engng., 61, (2), 189-193, (1983).

45. Eager, R. L., J.F. Mathews, J.C. Roy, and J.M. Pepper, "Chemical studies on oils derived from aspen poplar wood, cellulose, and an isolated aspen poplar lignin", *Can. J. Chem.*, 61, (9), 2010-2015, (1983).
46. Eager, R.L., J.F. Mathews and J.M. Pepper, "A continuous reactor for the liquefaction of aspen poplar", in Fifth Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 435-439 (1984).
47. Eager, R.L. and J.M. Pepper, "Study of screw reactor liquefaction", in Sixth Canadian Bioenergy R&D Seminar, C. Granger (ed.), 417-421, (1987).
48. Elliott, D.C., "Analysis and comparison of products from wood liquefaction", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne and L.K. Mudge, 1003-1018, (1982).
49. Elliot, D.C., L.J. Sealock and S.R. Butner, "Product analysis from direct liquefaction of several high-moisture biomass feedstocks" in Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series 376, Amer. Chem. Soc., Washington DC, 179, (1988).
50. Espenson, J.H., "Reaction and reaction rates", in Chemical Kinetics and Reaction Mechanism, McGraw-Hill, 1-8, 58-59, 1981.
51. Evans, R.J. and T. Milne, "Molecular-beam, Mass-spectrometric studies of wood vapour and model compounds over and HZSM-5 catalyst", in Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading, Denver, E.J. Soltes and T.A. Milne (eds.), 311-327, (1987).
52. Fengel, D. and G. Wegener, "Chemical composition and analysis of wood", in Wood: Chemistry, Ultrastructure, Reactions, Walter de Gruyter, 26-59, (1984).
53. Flanigen, E.M., J.M. Bennett, R.W. Grose, J.P. Cohen, R.L. Patton, R.M. Kirchner and J.V. Smith, "Silicalite, a new hydrophobic crystalline silica molecular sieve", *Nature*, 271, 512-516, (1978).
54. Fogler, H.S., Elements of Chemical Reaction Engineering, Prentice-Hall, 60-63, 203-207, 580-582, 1986.
55. Freel, B.A., R.G. Graham, M.A. Bergougnou, R.P. Overend and L.K. Mok, "The kinetics of fast pyrolysis (Ultrapyrolysis) of cellulose in a fast fluidized bed reactor, paper presented at AICHE Fluidization Section, Miami, Florida, (1986).

56. Froment, G.F. and K.B. Bischoff, "Fixed bed catalytic reactors", in Chemical Reactor Analysis and Design, John Wiley & Sons, New York, 532-546, 1979.
57. Funazukiri, T., R.R. Hudgins and P.L. Silveston, "Product distribution in pyrolysis of cellulose in a microfluidized bed", *J. Anal. Appl. Pyrolysis*, 9, 139-158, (1986).
58. Funazukuri, T., R.R. Hudgins and P.L. Silveston, "Product distribution for flash pyrolysis of cellulose in a coil pyrolyzer", *J. Anal. & Appl. Pyrol.*, 10, 225-249, (1987).
59. Furrer, R.M., "Direct conversion of plant oils and de-pitched tall oil to fuels and chemicals using HZSM-5 catalyst", Univ. of Saskatchewan, M.Sc. thesis, 48-51, (1988).
60. Garwood, W.E., P.D. Caesar, and J.A. Brennan, U.S. patent 4 150 062, (1979a).
61. Garwood, W.E., P.D. Caesar, and J.A. Brennan, U.S. patent 4 149 960, (1979b).
62. Goheen, D.W., "Low molecular weight chemicals in lignins", in Lignins: Occurrence, Formation, Structure and Reactions K.V. Sarkanen and C.H. Ludwig (eds.) Wiley-Interscience, New York, 803, (1971).
63. Graef, M., G.G. Allen and B.B. Krieger, "Product distribution in the rapid pyrolysis of biomass/lignin for production of acetylene", in Biomass as a Non-Fossil Fuel Source, ACS Symposium Series, 44, 293-311, (1981).
64. Graham, R.G., L.K. Mok, M.A. Bergougnou, H.I. de Lasa and B.A. Freel, "Fast pyrolysis (Ultrapyrolysis) of cellulose", *J. Anal. Appl. Pyrolysis*, 6, 363-374, (1984).
65. Graham, R.G., B.A. Freel and R.P. Overend, "Thermal and catalytic fast pyrolysis of lignin by rapid thermal processing (RTP)", in 7th Canadian Bio-energy R&D Seminar, NRC, Ottawa, 669-673, (1989).
66. Grainger, L. and J. Gibson, "Liquefaction of coal", in Coal Utilization, Technology, Economics and Policy, Kings English Book Printers, 211-218, (1981).
67. Guisnet, M., P. Magnoux, and C. Canaff, New Developments in Zeolite Science and Technology, Proc. 7th Int. Zeolite Conf., Y. Murakami, A. Iigima and J.W. Ward (eds.), Elsevier, 701-707, 1986.
68. Haag, W.O., P.G. Rodewald and P.B. Weisz, "Conversion of biological materials to liquid fuels", US Patent 4 300 009,

(1981).

69. Hall, C.W., "Biomass sources for fuel", in Biomass as an Alternative Fuel, 77, (1981).

70. Hallen, R.T., L.J. Sealock and R. Cuello, "Influence of alkali carbonates on biomass volatilization", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne and L.K. Mudge (eds.), 157-168, (1982).

71. Hayes, R.D., "Biomass pyrolysis technology and products: A Canadian viewpoint", in Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.) 8-15, (1988).

72. Hichmann, H.L., W.D. Turner, R. Hopper, F. Hasseris, J.L. Kuester and G.L. Frezek, "Pyrolytic conversion of municipal waste to energy", in Thermal Conversion Systems for Municipal Solid Wastes, Noyes Publications, 33-40, (1984).

73. Hornell, C., P. Bjornbom, E. Bjornbom, A. Bergstrom, G. Karlsson, O. Karlsson, B. Olsson, Y. Solantausta and B. Ahgren, "Dissolution of peat and wood in tetralin compared with coal", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne L.K. and Mudge (eds.) 827-838, (1982).

74. Ison, A. and R.J. Gorte, "The adsorption of methanol and water on HZSM-5", J. Catal., 89, 150-158, (1984).

75. "IVPRK/DIVPRK Differential Equations Solver", in IMSL Math/Library, 632-639, (1992).

76. Jamin, A., J.C. Lavalley, A. Macedo and F. Raatz, "FT-IR study of the Bronsted acid sites in dealuminated HY zeolites using specific probe molecules", in Perspectives in Molecular Sieve Science, W.H. Flank and T.E. Whyte Jr (eds.), 117-135, (1988).

77. Jezko, J. and J. Howard, "Supercritical fluid extraction of poplar wood in a continuous liquefaction unit", in Fifth Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 398-401, (1984).

78. Johnson, D.K. and H.L. Chum "Some aspects of pyrolysis characterization by high performance size exclusion chromatography (HPSEC)", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series, 32, 167-177, (1987).

79. Kaeding, W.W. and S.A. Butter, "Conversion of methanol and dimethyl ether", US Patent 3 911 041, (1975).

80. Kaliaguine, S., "Upgrading pyrolytic oils from wood and other biomasses", Contract No. 036-1326/0274, National Research Council of Canada, 6, 99-100, (1981).
81. Kaliaguine, S., Upgrading pyrolytic oils from wood, paper presented at Wood Liquefaction Specialists meeting, Saskatoon, 1-25, (1982).
82. Kallury, R.K., T.T. Tidwell, D.G.B. Boocock, F. Agblevor, M. Holysh and N. Sathi, "Studies on oils derived from the rapid hydrolysis of aspen poplar wood and cellulose", in Fifth Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 402-406, (1984).
83. Kam, E.K.T. and R. Hughes, "Non-isothermal fouling of catalyst pellets using Langmuir-Hinshelwood fouling kinetics", *AIChE*, 25 (2), (1979).
84. Kaminsky, W., H.J. Sinn and H. Timmann, "Industrial pyrolysis in a fluidised bed", in Recycle International: Recovery Energy Matter, Residues Waste, T. Kozmiensky and K.J. Freitag (eds.), Verlag Umwelttech, Berlin, FRG, 508-513, (1982).
85. Kang, C.C., G. Nongbri, and N. Stewart, "The effect of the solvent in the solvent refined coal process", in Liquids Fuels from Coal, Academic Press, 1-18, (1976).
86. Karlsson, O. and P. Bjornbom, "Characterization of peat and biomass liquids", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne and L.K. Mudge (eds.), 1019-1026, (1982).
87. Kocker, H. M-Z. and A. Nelte, "Two stage liquefaction process of biomass", in Energy from Biomass, 4, Proceedings of the Third Contractors Meeting, Paestum, G. Grassi, D. Pirrunitz and H. Zibetta (eds.), 593-597, (1988).
88. Klass, D.L., and C.T. Sen, "Energy from waste", *Chem. Eng. Prog.*, 83, 46-52, (1987).
89. Knight, J.A., C.W. Gorton, and R.J. Kovac, "Oil production by entrained flow pyrolysis of biomass", *Biomass* 6, 69-76, (1984).
90. Kwart, H. and K. King, "Rearrangement and cyclization reactions of carboxylic acids and esters" in The Chemistry of Carboxylic Acids and Esters, S. Patia (ed.), John Wiley & Sons, 341-373, 1969.
91. Leroy, J., L. Choplin and S. Kaliaguine, "Rheological characterization of pyrolytic wood derived oils: Existence of

- a compensation effect", *Chem. Eng. Comm.*, 71, 157-176, (1988).
92. Levenspiel, O., Chemical Reaction Engineering, 2nd edition, John Wiley & Sons, 6, 32, 69-71, 483-484, (1971).
93. Mathews, J.F., M.J. Tepylo, R.L. Eager and J.M. Pepper, "Upgrading of aspen poplar wood oil over HZSM-5 zeolite catalyst", *Can. J. Chem. Eng.*, 63, 686-689, (1985).
94. March, J., Advanced Organic Chemistry: Reactions, Mechanisms and Structure. McGraw-Hill, New York, 620, 1977.
95. McDonald, E., B. Bennet and J. Howard, "Liquefaction of international energy agency (IEA) poplar wood and peat by supercritical fluid extraction", in Fifth Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 393-397, (1984).
96. McMillen, D.F., R. Malhotra and E.S. Nigenda, "The case for induced bond scission during coal pyrolysis" in Producing, Analyzing and Upgrading of Oils from Biomass, Symposium sponsored by Div. Fuel Chem. at the 194th Meeting of the Amer. Chem. Soc. at New Orleans LA, 32(3), 180, (1987).
97. Meier, D. and O. Faix, "Effect of hydrogen pressure on yields and quality of oils obtained from direct liquefaction of pine wood", in Energy from Biomass, 4, Proceeding of the Third Contractors Meeting, Paestum, G. Grassi, D. Pirrunitz and H. Zibetta (eds.), 584-592, (1988).
98. Michiels, P. and O.C.E. De Herdt, Molecular Sieve Catalysts, Pergamon Press, 40-45, 69-71, 212-213, 1987.
99. Molton, P.M., T.F. Demmitt, J.M. Donovan and R.K. Miller, "Mechanism of conversion of cellulose wastes to liquid fuels in alkaline solution", in Energy from Biomass and Wastes III. Inst. Gas Technol., D.L. Klass (ed.), Chicago IL, 293-316, (1978).
100. Moore, J.W. and R.G. Pearson, Kinetics and Mechanism, John Wiley & Sons, New York, 1-80, 1981.
101. Morrison, R.T. and R.N. Boyd, "Functional derivatives of carboxylic acids", in Organic Chemistry, Allyn and Bacon, 659-664, 1966.
102. Oudejans, J.C., P.F. Van DenOosterkamp and V. Bekkum, "Conversion of ethanol over zeolite H-ZSM-5 in the presence of water", *Appl. Catal.*, 3, 109-115, (1982).
103. Pakdel, H., and C. Roy, "Chemical characterization of wood oils obtained in a vacuum pyrolysis process development unit", in Pyrolysis Oils From Biomass: Producing, Analyzing

- and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series, 32, 203-214, (1987).
104. Peters, W.A., "Studies of the pyrolysis behaviour of condensed phase fuels with applications to fuel conversion technology", in Analytical Pyrolysis, K.J. Voorhies (ed.), Butterworths, 349-406, (1984).
105. Petersen, E.E. and A.T. Bell, "Fouling of catalysts" in Catalyst Deactivation, Marcel Dekker, New York, 41-47, 1987.
106. Pines, H., "Acid-catalyzed reactions" in The Chemistry of Catalytic Hydrocarbon Conversions, Academic Press, 85-95, 1981.
107. Pober, K.W. and H.F. Bauer, "The nature of pyrolytic oil from municipal wastes", in Fuels from Wastes, L.L. Anderson and D.A. Tillman (eds.), 73-85, (1977).
108. Prasad, Y.S., N.N. Bakhshi, R.L. Eager and J.F. Mathews, "Effect of steam addition on catalytic upgrading of canola oil", Catalysis on the Energy Scene, 85-92, (1984).
109. Prasad, Y.S., N.N. Bakhshi, J.F. Mathews and R.L. Eager, "Catalytic conversion of canola oil to fuels and chemical feedstocks. Part II. Effect of co-feeding steam on the performance of HZSM-5 catalyst", Can. J. Chem. Eng., 64, (2), 285-292, (1986).
110. Prasad, Y.S., H. Yaoliang and N.N. Bakhshi, "Effect of hydrothermal treatment of HZSM-5 catalyst on its performance for the conversion of canola and mustard oils to hydrocarbons", Ind. Eng. Chem. Prod. Res. Dev., 25, 251, (1986).
111. Probststein, R.F. and R.E. Hicks, "Chemistry for Synthetic Fuels", in Synthetic Fuels, McGraw-Hill Book Company, 31-42, 1982.
112. Pryor, W.A., Free Radicals. McGraw-Hill, New York, 58, 1966.
113. Radlein, D., J. Piskorz, A. Grinshpun, and D.S. Scott, "Fast pyrolysis of pre-treated wood and cellulose", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series, 32, 29-35, (1987).
114. Reed, T.B. and C.D. Cowdery, "Heat flux requirements for fast pyrolysis and a new method for generating biomass vapour", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS

Symposium Series, 32, 68-81, (1987).

115. Renaud, M., P.D. Chantal and S. Kaliaguine, "Anisole production by alkylation of phenol over ZSM-5", *Can. J. Chem. Eng.*, 64, 5, 787-791, (1986).

116. Renaud, M., J.L. Grandmaison, C.H. Roy and S. Kaliaguine, "Conversion of vacuum pyrolytic oils from populus deltoides over HZSM-5" in Producing, Analyzing, and Upgrading Of Oils From Biomass, 276, (1987).

117. Renaud M., J.L. Grandmaison, C. Roy, and S. Kaliaguine S., "Low pressure upgrading of vacuum pyrolysis oils from wood", in Pyrolysis Oils from Biomass: Producing, Analyzing, and Upgrading, ACS Symp. Ser., 290-310, (1988).

118. Roy, C., B. de Caumia, J. Yang and P. Plante, "Evaluation of the vacuum pyrolysis process-Biomass as a case study", in 7th Canadian Bio-energy R&D Seminar, NRC, Ottawa, 675-679, (1989).

119. Schulz, H., W. Bohringer, W. Baumgartner and Z. Siwei, "Comparative investigation of time-on-stream selectivity changes during methanol conversion on different zeolites", in, New Developments in Zeolite Science and Technology, proceedings of 7th International Zeolite Conference, Y. Murakami, A. Iijima and J.W. Ward (eds.), Tokyo, 915-922, (1986).

120. Scott, D.S. and J. Piskorz, "The flash pyrolysis of aspen poplar wood", *Can. J. Chem. Eng.*, 60, 666-674, (1982).

121. Scott, D.S. and J. Piskorz, "The Waterloo Fast Pyrolysis Process for the production of liquids from biomass", in 5th Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), 407-412, (1984).

122. Scott, D.S., J. Piskorz and D. Radlein, "Liquid products from the continuous flash pyrolysis of biomass", *Ind. Eng. Chem. Proc. Des. Dev.*, 24, 581-588, (1985).

123. Scott, D.S. and J. Piskorz, "The role of temperature in the fast pyrolysis of cellulose and wood", *Ind. Eng. Chem. Res.*, 27, 8-15, (1988).

124. Scott, D.S., J. Piskorz, I.B. Westerberg and P. McKeough, "Flash pyrolysis of peat in a fluidized bed" *Fuel Processing Tech.*, 18, 81-95, (1988).

125. Scott, D.S., J. Piskorz, D. Radlein, P. Majerski, and S. Czernik, "New developments in the Waterloo Fast Pyrolysis process", in 7th Canadian Bio-energy R&D Seminar, NRC, Ottawa,

699-702, (1989).

126. Scott, J., Zeolite Technology and Applications: Recent Advances, Noyes Data Corporation, 27-58, 174-198, 1980.

127. Sharma, R.K. and N.N. Bakhshi, "Upgrading of biomass-derived pyrolytic oils over HZSM-5 catalyst", Report of Contract File No. 058SZ-23283-8-6116, Renewable Energy Branch, Energy, Mines and Resources, Canada, (1989).

127. Sharma, R.K. and N.N. Bakhshi, "Upgrading of wood-derived bio-oil over HZSM-5", Biores. Tech., 35, 57-66, (1991a).

128. Sharma, R.K. and N.N. Bakhshi, "Catalytic conversion of crude tall-oil to fuels and chemicals over HZSM-5: Effect of co-feeding steam", Fuel Processing Technology, 27, 113-130, (1991b).

129. Sharma, R. K. and N.N. Bakhshi, "Catalytic conversion of tall oil to fuels and chemicals over HZSM-5 using various diluents", in Energy from Biomass and Wastes XIV, Klass D.L. (ed.), 1033-1061, (1991c).

130. Sharma, R.K., and N.N. Bakhshi,, "Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals", Can. J. Chem. Eng., 69, 1071-1081, (1991d).

131. Sheppard, W.J. and E.S. Lipinsky, "Chemicals from biomass", in Biomass Utilization, W.A. Cote (ed.), Life Sciences Series, 67, 635-658.

132. Sheu, Y.H.E., R.J. Anthony and E.J. Soltes, "Kinetic studies of upgrading pine pyrolytic oil by hydrotreatment", Fuel Proc. Technol., 19, 31-50, (1988).

133. Sjostrom, E., Wood Polysaccharides, in Wood Chemistry: Fundamentals and Applications, Academic Press, 49-62, 1981.

134. Smith, J.M, "Kinetics of fluid-solid catalytic reactions", in Chemical Engineering Kinetics, 2nd edition, McGraw-Hill, 329-352, (1970).

135. Soltes, E.D., "Thermochemical route to chemicals, fuels and energy from forestry and agricultural residues", in Biomass Utilization, W.A. Cote (ed.), Life Sciences Series, 67, 537-552, (1983).

136. Soltes, E.D., "Cellulose: Elusive component of the plant cell wall", in Biomass Utilization, W.A. Cote (ed.), Life Sciences Series, 67, 271-292, (1983).

137. Soltes, E.J. and S-L. Lin, "Chromatography of non-

derivatized pyrolysis oils and upgraded products", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series, 264, 178-185, (1987).

138. Soltes, E.J., S-L. Lin and Y-H. E. Sheu, "Catalyst specificities in high pressure hydroprocessing of pyrolysis and gasification tars", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series, 264, 229-239, (1987).

139. Soveran, D.W. and W. Craig, "Conversion of biomass-derived oil to valuable transportation fuel blending components", in 5th European Conference on Biomass for Energy and Industry-Abstract, Lisbon, Portugal, 04.02, (1989).

140. Steinberg, M.P., P.T. Fallon and M.S. Sundaram, "Flash pyrolysis of biomass with reactive and non-reactive gases", Summary Report, Proc. Sci. Div., Brookhaven National Lab., New York, USA, Dec. (1986).

141. Strayer, R.C., G.C. Zoerb, W. Craig, J. Blake and F.B. Dyck, "Canola oil as fuel for farm diesel engines", in 5th Canadian Bioenergy R&D Seminar, S. Hasnain (ed.), Elsevier Appl. Sci. Publ., London, 512-515, (1984).

142. Sundaram, M.S., M. Steinberg and P.T. Fallon, "Flash pyrolysis of biomass with reactive and non-reactive gases", in Fundamentals of Thermochemical Conversion, R.P. Overend, T.A. Milne and L.K. Mudge, 167-182, (1982).

143. Swinbourne, E.S., "Rate and Order", in Analysis of Kinetic Data, Nelson & Sons, 51-64, 1971.

144. Szostak, R., Molecular Sieves: Principles of Synthesis and Identification, Van Nostrand Reinhold, New York, 15-45, 379, 394, 398, 1989.

145. Taylor, W.I. and A.R. Battersky, Oxidative Coupling of Phenols. Dekker, New York, 1, 1967.

146. Tillman, D.A., "The value of wood", in Wood as an Energy Resource, Academic Press, 65-85, 1978.

147. Topsoe, N-Y., K. Pedersen and E.G. Derouane, "Infrared and Temperature-programmed desorption study of the acidic properties of ZSM-5-type zeolites", J. Catal., 70, 41-52, (1981).

148. Vasilakos, N.P. and D.M. Austgen, "Hydrogen-donor solvents in biomass liquefaction, Ind. Eng. Chem. Proc. Des. Dev., 24 304-311, (1985).

149. Waddams, A.L., "Petroleum chemical products and their applications", in Chemicals From Petroleum, Gulf Publishing Company, London, 251-282, 1980.
150. Westerterp, K. R., W.P.M. van Swaaij and A.A.C.M. Beenackers, Chemical Reactor Design and Operation, John Wiley & Sons, 14-24, 1984.
151. Weisz, P.B., W.O. Haag, and P.G. Rodewald, "Catalytic production of high-grade fuel (gasoline) from biomass compounds by shape-selective catalysis", *Science*, 206, 57-58, (1979).
152. White, D.H., D. Wolf and Y. Zhao, "Biomass liquefaction utilizing extruder-feeder reactor systems", in Pyrolysis Oils From Biomass: Producing, Analyzing and Upgrading, E.J. Soltes and T.A. Milne (eds.), ACS Symposium Series, 32, 106-116, 1987.
153. Wojciechowski, B.W. and A. Corma, "Kinetics of gas-oil cracking", in Catalytic Cracking: Catalysts, Chemistry and Kinetics, Marcel Dekker, 1-20, 201-222, 1986.
154. Wu C.N., "Aldehydes and Ketones" in Modern Organic Chemistry, Barnes & Noble, 324, 1979.
155. Zinkel, D.F., "Stability of tall oil precursors in black liquor", *Tappi*, 60, (2), 129-130, (1977).

Appendix A: X-RAY POWDER DIFFRACTION

A1: X-ray powder diffraction data for the zeolites structures used in this research that appear in the literature. Listing of most intense peaks in order of decreasing intensity [Szostak, 1989].

| Catalyst | Patent | Peak Position, d(A°) |
|-------------------|-----------------------------|--|
| ZSM-5 | Mobil US3702886 | 3.84, 3.74, 3.62, 11.36, 10.20 |
| Silicalite | Union Carbide US4061724 | 11.1, 10.02, 3.85, 3.82, 3.71, 3.74 |
| Mordenite | | 9.03, 3.98, 3.386, 4.51, 13.52, 6.38, 2.697 |
| Y-type zeolite | Union Carbide, US3130007 | 14.29, 2.858, 3.775, 5.68, 3.308, 4.38 |

Appendix B: Chromatography Section

B1: Typical chromatograph obtained from upgrading wood-oil over HZSM-5. Compound identification is made by retention time (RT) and presented in the table following.

B2:

| Compound | RT, min | Compound | RT, min |
|--------------------------------------|------------|---|------------|
| Cyclopentane, 1-methyl-2-methylene- | 2.46 | 1H-Indene | 17.54 |
| 1,4-Heptadiene, 3-methyl- | 2.65 | Phenol, 4-methyl- | 17.72 |
| 1,4-Hexadiene, 3-methyl- | 2.93 | Benzene, 1-methyl-2-(2-propenyl)- | 17.96 |
| Benzene | 3.91 | 1H-Indene, 2,3-dihydro-1-methyl- | 18.36 |
| Benzene, ethyl- | 6.53 | Naphthalene, decahydro- | 18.57 |
| Cyclopentene, 1-ethenyl-3-methylene- | 8.36 | 3-Non-5-yne, 4-ethyl- | 18.76 |
| Cyclohexene, 3,5,5-trimethyl- | 9.45 | Phenol, 2,6-dimethyl- | 19.52 |
| Benzene, 1,4-dimethyl- | 10.42 | Phenol, 2,3-dimethyl- | 20.52 |
| Furan, 4-methyl-2-propyl- | 10.51 | Benzene, 1-methyl-4-(1-propenyl)- | 20.69 |
| Benzene, (1-methylethyl)- | 11.25 | Naphthalene, 1,2,3,4-tetrahydro- | 21.71 |
| Bicyclo[5.2.0]non-1-ene | 12.57 | Benzene, (2-methyl-1-methylenepropyl)- | 22.11 |
| Benzene, propyl- | 12.98 | 1H-Indene, 1-methylene- | 22.43 |
| Benzene, 1-ethyl-3-methyl- | 13.77 | Benzene, (1,1-dimethyl-2-propenyl)- | 22.67 |
| Phenol | 14.09 | Naphthalene, 1,2-dihydro-3-methyl- | 23.54 |
| Cyclohexanone, 2,3-dimethyl- | 14.16 | Naphthalene, 1,2,3,4-tetrahydro-5-methyl- | 23.86 |
| Benzene, 1,3,5-trimethyl- | 14.87 | 1H-Indene, 1-ethylidene- | 24.80 |
| Benzene, 1-ethenyl-2-methyl- | 16.79 | Naphthalene, 1,7-dimethyl- | 25.65 |

Appendix C: KARL FISCHER TITRATION AND SYNTHESIS OF H-ZSM-5 CATALYST

C.1 Karl Fischer (KF) Titration

The procedure followed in this work is as follows:

1. Dissolve samples of the wood-oil or organic liquid product in AQUASTAR SOLVENT S, a two component KF solvent or AQUASTAR SOLVENT K, a two component KF solvent for samples containing aldehydes and ketones which can interfere by reacting with methanol contained in the KF reagent.

2. Titrate with KF reagents, AQUASTAR TITRANT 5 when using solvent S and AQUASTAR TITRANT 5K when using solvent K. AQUASTAR TITRANT S is a two component, pyridine free KF reagent and AQUASTAR TITRANT 5K is a two component pyridine free reagent which is used for samples containing aldehydes or ketones. In both cases 1 mL of titrant is equivalent to 4 mg water.

The measurement procedure is as follows:

1. 20 mL of the solvent is pipetted into a titration vessel.
2. Titration is carried out until a constant end point, detected electrometrically, is reached. The solvent and titration vessel are pre-dried.
3. The sample is placed in the titration vessel.
4. The water content is titrated with titrant. A Beckman Expanded Scale pH Meter was used for detecting the end point.

C.2 Synthesis of HZSM-5 Catalyst

The procedure outlined by Chen et al. [1973] was followed in synthesizing the HZSM-5 catalyst used in this work.

Chemicals Used

- A. Sodium aluminate (43.5 wt% aluminium oxide, 30 wt% sodium oxide, and 26.5 wt% water) from Fisher Scientific.
- B. Sodium hydroxide pellets from BDH.
- C. Sodium metasilicate (28.5 wt% silica oxide, 7.7 wt% sodium oxide and 63.7 wt% water) from Fisher Scientific.
- D. Tetrapropylammonium bromide from Aldrich.
- E. Sulfuric acid from BDH.
- F. Sodium chloride from BDH
- G. Hydrochloric acid from BDH.
- I. Silver nitrate solution.

Equipments Used

- A. 3-L Flat bottomed flask.
- B. Condenser.
- C. Large magnetic stirrer and heater.
- D. High speed blender, Osterizer, 1.5 L.
- E. 100 mL graduated cylinder (Solution A).
- F. Two 250 mL beakers (Solution C and E).
- G. 150 ml beaker (Solution D).
- H. 1 L beaker (Solution B).
- I. Larger magnetic stirrer.
- J. Hourglass.
- K. Glass stirring rod.
- L. 2 L Filtering flask.
- M. 18 cm diameter Buckner funnel.
- N. Waterman filtering paper, ashless, 15 cm.
- O. 4 L Beaker.
- P. Air Blower.

Procedure

1. Prepare the following solutions:

Solution A:

- 2.5 g sodium aluminate
- 0.17 g sodium hydroxide
- 66.0 g distilled water

Appearance: Clear, Volume approximately 66 cc.

Solution B:

- 211.2 g sodium metasilicate (150 cc)
- 264 g distilled water

Appearance: Clear.

Solution C:

- 26.4 tetrapropylammonium bromide
- 132 g distilled water

Appearance: Clear.

Solution D:

- 21.0 g sulfuric acid
- 66 g distilled water

Appearance: Clear.

Solution E:

- 79.2 g sodium chloride
- 95 g distilled water

Appearance: Slurry and white.

2. Solutions B,C,D,E are then mixed as follows:

- add solution B to blender, the mixture will become pure white; use the blower to keep the blender cool if necessary.
- with blender at highest speed add consecutively solutions C and E, each at once.

- then add solution D at approximately 1 cc/5 sec.
 - continue mixing for approximately 10 min.
 - the mixture remains a liquid white.
3. Transfer the reaction mixture to the 3 L flat bottomed flask, switch heater on and turn on the magnetic stirrer for a maximum agitation (no sediments must be seen).
 4. Fine tune the heater setting until minimum refluxing is attained and the reaction mixture is maintained at 100 °C. Wrap the flask with pyrex wool.
 5. Once steady state has been attained, add 10 % by volume of solution A to reaction mixture. This concludes day 1.
 6. In 24 h intervals beginning from step 5, add 10 % of the remaining A solution two more times (days 2 to 3, followed by 7 additions of 57 % of the remaining portion of solution A (days 5 to 10). Hence, covering an additional period of nine days.
 7. After 10 days switch off the magnetic stirrer and the heater, allow the mixture to cool to room temperature (approx. 4.5 h).
 8. Carefully filter the reaction mixture through fast qualitative filter paper under vacuum. Clean the flask out with distilled water, saving as much ZSM-5 as possible. Filtration takes roughly 1.5 h.
 9. Wash the crystals 3 times with hot distilled water carefully, followed once by cold distilled water. A total of approximately one L should be used. The ZSM-5 will appear as a thick white paste.
 10. Place the Buckner funnel with the ZSM-5 in the oven to dry at 100 °C for a minimum of 1 h.
 11. Transfer the ZSM-5 to a crucible, removing the filter paper, and place it in the furnace for 16 h at 550 °C to remove the organic template.

Ion-exchange to Produce HZSM-5

12. Prepare a 2.0 L solution of 0.5 M HCl; also, clean out the flask with concentrated solution of NaOH, then distilled water. Pour the 2.0 L HCl solution into the flask, switch on the stirrer and heater. A 0.5 M solution of HCl can be prepared by adding 84 cc of concentrated HCl to distilled water to make 2 L.
13. Allow the ZSM-5 (Approx. 64 g) to cool, then return it to

the 3-L flat bottomed flask into which has been added 2.0 L of 0.5 M HCl. The mixture is then refluxed at 80 °C for 24 h.

14. Allow the solution to cool and then filter as in steps 8 and 9. Continue to wash the crystals until the filtrate is free of Cl⁻ ions. A white precipitate will form with the silver nitrate solution if Cl⁻ ions are present.

15. Then place the crystals in the oven at 110 °C for 1 h to dry, followed by 4 h in the furnace at 400 °C.

16. Once cooled the catalyst can be crushed (place in dye and pressurize to roughly 10000 psi for 1 min) and sieved to the desired size range.

Appendix D: EXPERIMENTAL DATA

D.1 Major compounds identified in the volatile fraction of the wood-oil on different days and temperatures (172 Pa).

| Time, Days | 1 | | | 16 | | | | 31 | | |
|---|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | Temperature, °C | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 |
| <u>Acids and Esters</u> | | | | | | | | | | |
| Formic acid, 1-methylpropyl ester- | --- | --- | --- | 0.2 | 0.3 | 0.5 | 0.1 | 0.2 | 0.1 | |
| Acetic acid, methyl ester- | 0.2 | 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 0.2 | 0.3 | 0.1 | |
| 3-Propanoic acid | 0.9 | 0.8 | 0.5 | 0.8 | 0.6 | 0.8 | 0.1 | 0.1 | 0.1 | |
| Carbonic acid, phenylester- | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.1 | 0.5 | 0.3 | 0.5 | |
| Carbonic acid, dihexylester- | 0.8 | 0.7 | 0.6 | --- | --- | --- | --- | --- | --- | |
| <u>Alcohols</u> | | | | | | | | | | |
| Cyclopentanol | 0.5 | 0.3 | 0.1 | 1.3 | 1.0 | 0.6 | 0.8 | 0.9 | 0.8 | |
| Cyclopentanol, 2-methyl- | 0.3 | 0.9 | 2.1 | 0.2 | 0.3 | 0.9 | --- | --- | --- | |
| Cyclohexanol, 4-methyl, cis- | 1.9 | 1.9 | 2.3 | --- | --- | --- | --- | --- | --- | |
| Cyclohexanol, 1-methyl-4-(1-methylethenyl)- | --- | --- | --- | 0.9 | 1.1 | 0.9 | 0.6 | 0.7 | 0.6 | |

Appendix D.1 continued.

| Time, Days | 1 | | | 16 | | | | 31 | | |
|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|--|
| Temperature, °C | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 | |
| <u>Aldehydes & ketones</u> | | | | | | | | | | |
| Cyclopentanone, 2-methyl- | 3.1 | 1.3 | 1.1 | 1.7 | 1.0 | 0.4 | --- | --- | --- | |
| Cyclopentene-1-one, 2-hydroxy-3-methyl- | --- | --- | --- | 8.1 | 5.5 | 3.2 | 5.8 | 5 | 2.1 | |
| Hexanal, 4-methyl- | 1.1 | 1.2 | 1.0 | --- | --- | --- | --- | --- | --- | |
| Cyclopentanone, 1-methyl-2-propyl- | 2.5 | 1.6 | 1.2 | --- | --- | --- | --- | --- | --- | |
| Cyclohexanone, 2-ethyl-2-propyl- | 2.7 | 1.8 | 1.5 | 3.9 | 3.6 | 2.8 | 2.5 | 1.2 | 0.3 | |
| <u>Non-cyclic Aliphatic Hydrocarbons</u> | | | | | | | | | | |
| Pentane, 3-ethyl-2,2-dimethyl- | 0.2 | 0.2 | 0.2 | 0.7 | 0.6 | 0.5 | 0.7 | 0.6 | 0.4 | |
| 1,7-Octadiene, 2,7-dimethyl- | 1.1 | 0.6 | 0.6 | 0.1 | --- | --- | 0.4 | 0.1 | --- | |
| 3-Octyne, 5-methyl- | 1.1 | 0.6 | 0.5 | 0.2 | 0.1 | --- | 0.3 | 0.1 | 0.1 | |

Appendix D.1 continued.

| Time, Days | 1 | | | 16 | | | | 31 | | |
|------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|--|
| Temperature, °C | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 | |
| <u>Aromatic Hydrocarbons</u> | | | | | | | | | | |
| Benzene, cyclopropyl- | 1.9 | 1.7 | 1.6 | 1.6 | 1.5 | 1.9 | 0.5 | 0.3 | 0.2 | |
| Benzene, (1-ethyl-2-methyl)- | --- | --- | --- | 2.9 | 2.4 | 1.9 | 3.6 | 3.0 | 2.5 | |
| Benzene, 2-butenyl- | 4.3 | 3.8 | 3.6 | 3.4 | 2.1 | 2.0 | 1.7 | 1.8 | 1.7 | |
| Benzene, 1-ethyl-4-methyl- | 2.2 | 0.8 | 0.7 | --- | --- | --- | --- | --- | --- | |
| Benzene, (1,1-dimethyl-2-propyl)- | --- | --- | --- | 1.3 | 1.8 | 1.4 | 1.3 | 1.9 | 1.8 | |
| Phenanthrene, methyl- | 1.2 | 1.2 | 1.3 | 1.1 | 1.0 | 1.1 | 0.9 | 0.8 | 0.6 | |
| <u>Ethers & Furans</u> | | | | | | | | | | |
| Benzene, 1-methoxy- | 1.4 | 0.7 | 0.6 | 2.9 | 1.9 | 2.1 | 3.6 | 2.6 | 2.8 | |
| Benzene, 1-ethoxy- | 3.4 | 2.5 | 2.4 | --- | --- | --- | --- | --- | --- | |
| Furan, 2,3-dihydro-1-methylethyl)- | 2.6 | 2.1 | 2.0 | 1.0 | 1.7 | 1.6 | 2.5 | 3.3 | 3.5 | |
| Benzofuran, 2,3-dihydro-2-methyl- | 0.4 | 0.6 | 0.7 | 2.0 | 1.5 | 1.3 | 0.5 | --- | --- | |

Appendix D.1 continued.

| Time, Days | 1 (Fresh wood-oil) | | | 16 | | | 31 | | |
|--|-----------------------|------|------|------|------|------|------|------|------|
| | 175 | 200 | 250 | 175 | 200 | 250 | 175 | 200 | 250 |
| <u>Cyclic Aliphatic Hydrocarbons</u> | | | | | | | | | |
| Cyclopentane, 1-methyl-2-propyl- | 3.4 | 3.5 | 3.0 | --- | --- | --- | --- | --- | --- |
| Cyclopentane, 2-ethyl-1,1-dimethyl- | --- | --- | --- | 0.6 | 0.6 | 0.4 | 1.3 | 1.8 | 1.2 |
| Bicyclo[3.1.1]heptane, 6,6-dimethyl-3-methylene- | 3.0 | 1.5 | 1.5 | 2.9 | 1.6 | 1.6 | 4.8 | 3.5 | 3.0 |
| <u>Phenols</u> | | | | | | | | | |
| Phenol | 2.6 | 1.9 | 1.7 | 0.8 | 0.4 | 0.3 | 0.4 | 0.3 | 0.3 |
| Phenol, 4-methyl- | 4.0 | 1.6 | 1.9 | 0.7 | 0.6 | 0.4 | 0.7 | 0.6 | 0.3 |
| Phenol, 2-methoxy-4-propyl- | 1.6 | 0.4 | 0.5 | --- | --- | --- | --- | --- | --- |
| Phenol, 2-methoxy-4-2-propenyl- | 5.9 | 23.0 | 28.3 | 14.5 | 17.1 | 19.5 | 12.4 | 16.8 | 18.6 |
| Phenol, 2-ethyl-5-methyl- | --- | --- | --- | 1.2 | 1.4 | 1.6 | 1.8 | 1.4 | 1.6 |

D.2 Effect of temperature on yield (wt%) of major hydrocarbon compounds identified in organic distillate obtained from non-catalytic treatment of wood-oil in the presence and absence of steam.

| Co-feeding Steam | | | |
|------------------------------|-----------------|-----|-----|
| Compound | Temperature, °C | | |
| | 330 | 370 | 410 |
| 1,4-Heptadiene, 3-methyl- | 1.8 | 1.3 | 0.5 |
| 1,7-Octadiene, 2,7-dimethyl- | 2.7 | 0.9 | 3.6 |
| 1-Heptene, 6-methyl- | --- | 1.5 | --- |
| 1-Octene, 7-methyl- | 0.6 | 0.4 | 0.6 |
| Benzene, ethyl- | 0.7 | 0.5 | 0.8 |
| Benzene, propenyl- | 0.9 | 1.0 | 1.4 |
| Benzene, 1-ethenyl-2-methyl- | 1.4 | 0.9 | 1.4 |
| Benzene, 1-ethenyl-4-ethyl- | 2.6 | 2.8 | 2.7 |
| Anthracene | 0.2 | 0.2 | 0.4 |
| Phenanthrene, methyl- | 0.4 | 0.9 | 0.6 |

| No Steam | | | |
|-------------------------------------|-----------------|-----|-----|
| Compound | Temperature, °C | | |
| | 330 | 370 | 410 |
| Cyclopentane, 1-methyl-2-methylene- | 0.4 | 0.3 | 0.7 |
| Cyclopentane, 2-ethyl-1,1-dimethyl- | 0.4 | --- | --- |
| Benzene | 0.2 | 1.8 | 2.1 |
| Benzene, ethyl- | 2.2 | 1.7 | 1.2 |
| Cyclohexane, 3,5,5-trimethyl- | 0.9 | 0.4 | 0.9 |
| Benzene, propyl- | 1.1 | 2.0 | --- |
| Benzene, 1-ethyl-2-methyl- | --- | 3.5 | 3.0 |
| Benzene, 1,3,5-trimethyl- | --- | --- | 2.2 |
| Cyclooctane, pentyl- | 0.9 | 0.4 | 0.4 |
| Naphthalene, 1-methyl- | 0.2 | 0.2 | 0.5 |

D.3 Effect of process time on the composition of organic distillate obtained from upgrading over HZSM-5 in the presence and absence of steam.

| Process Time, min | | 15 | 30 | 45 | 60 |
|------------------------|----|-------|-------|-------|-------|
| Acids & Esters | NS | --- | --- | --- | --- |
| | S | --- | --- | --- | --- |
| Alcohols | NS | 1.1 | 2.1 | 1.1 | 1.1 |
| | S | 3.1 | 2.6 | 2.7 | 3.2 |
| Aldehydes & Ketones | NS | 6.7 | 4.3 | 4.2 | 5.1 |
| | S | 4.7 | 6.7 | 6.3 | 6.7 |
| Aliphatic Hydrocarbons | NS | 3.9 | 4.0 | 6.0 | 6.6 |
| | S | 2.4 | 1.7 | 3.3 | 4.1 |
| Aromatic Hydrocarbons | NS | 62.2 | 66.7 | 60.6 | 55.7 |
| | S | 59.1 | 58.5 | 57.3 | 53.9 |
| Furans | NS | 0.7 | 0.8 | 1.3 | 1.4 |
| | S | 2.2 | 1.7 | 2.6 | 2.9 |
| Naphthenes | NS | 4.4 | 4.4 | 5.1 | 5.3 |
| | S | 5.1 | 5.6 | 4.5 | 5.1 |
| Phenols | NS | 8.3 | 8.2 | 8.1 | 8.2 |
| | S | 10.8 | 11.9 | 10.1 | 9.4 |
| Unidentified Fraction | NS | 12.7 | 9.5 | 13.1 | 16.7 |
| | S | 12.6 | 11.3 | 13.2 | 14.7 |
| Total | NS | 100.0 | 100.0 | 100.0 | 100.0 |
| | S | 100.0 | 100.0 | 100.0 | 100.0 |

D.3 Effect of process time on yield of major hydrocarbon compounds identified after upgrading wood-oil (wt% of wood-oil).

With Steam

| Compound | Run time, min | | | |
|---|---------------|------|------|------|
| | 15 | 30 | 45 | 60 |
| Hexane | 0.02 | 0.03 | 0.10 | 0.15 |
| Benzene | 1.92 | 2.90 | 3.90 | 1.40 |
| Benzene, methyl- | 2.50 | 1.70 | 2.80 | 1.30 |
| Xylenes (o+m+p) | 2.80 | 6.80 | 2.50 | 1.10 |
| Benzene, 1,3,5-trimethyl- | --- | 0.90 | --- | --- |
| Benzene, 1-propenyl- | 0.07 | 0.37 | --- | --- |
| Cyclopentane, 1-methyl-2-methylene- | 0.60 | 0.02 | 0.30 | --- |
| Benzene, (2-methyl-2-propenyl)- | 0.40 | 0.70 | 0.70 | 0.65 |
| Cyclohexene, 1-methyl-3-(1-methylethyl)-cis | 0.50 | 0.09 | 0.20 | 0.40 |
| Benzene, 1-ethyl-4-ethenyl- | 0.53 | 0.52 | 0.50 | 0.50 |
| Benzene, (2-methyl-1-methylene propenyl)- | 0.70 | 1.60 | 1.40 | 1.20 |
| Benzene, (1,1-dimethyl-2-propenyl)- | 0.20 | 0.20 | 0.15 | 0.10 |

Appendix D.3 continued.

Without Steam

| Compound | Run time, min | | | |
|---|---------------|------|-----|-----|
| | 15 | 30 | 45 | 60 |
| Benzene | 4.6 | 3.2 | 2.2 | 0.6 |
| Benzene, methyl- | 7.8 | 8.5 | 8.4 | 6.1 |
| Benzene, ethyl- | 0.2 | 3.3 | --- | --- |
| Xylenes, (o+m+p) | 8.8 | 10.3 | 9.5 | 7.6 |
| Benzene, 1-propenyl- | 0.1 | 0.6 | --- | --- |
| Bicyclo[3.1.1]heptane dimethyl-3-methylene | 0.3 | 0.2 | 0.5 | 0.3 |
| Benzene, (2-methyl-2- propenyl)- | 1.1 | 1.1 | 1.2 | 1.0 |
| Benzene, 1-ethenyl-4- ethyl- | 0.5 | 0.8 | 0.7 | 0.7 |
| 3-Non-5-yne, 4-ethyl-, [E]- | 0.9 | 1.0 | 1.2 | 1.4 |
| Naphthalene, decahydro- | 0.3 | 0.6 | 0.4 | 0.3 |
| Benzene, (1-methyl-2- cyclopropen-1-yl)- | 0.6 | 0.9 | 0.6 | 0.5 |
| Benzene, (2-methyl-1- methylene propyl)- | 2.1 | 2.4 | 2.3 | 2.1 |

D.4 Effect of temperature on the composition of organic distillate obtained from upgrading over HZSM-5 in the presence and absence of steam.

| Temperature, °C | | 290 | 330 | 350 | 370 | 390 | 410 |
|------------------------|----|-------|-------|-------|-------|-------|-------|
| Acids & Esters | NS | --- | --- | --- | --- | --- | --- |
| | S | --- | --- | --- | --- | --- | --- |
| Alcohols | NS | 1.2 | 4.1 | 4.5 | 4.3 | 4.2 | 4.3 |
| | S | 3.9 | 2.9 | 2.6 | 2.6 | 2.9 | 3.9 |
| Aldehydes & Ketones | NS | 5.9 | 4.1 | 4.5 | 4.3 | 4.2 | 6.5 |
| | S | 8.8 | 7.8 | 7.8 | 6.7 | 5.8 | 4.8 |
| Aliphatic Hydrocarbons | NS | 3.2 | 3.2 | 3.7 | 4.0 | 3.9 | 2.7 |
| | S | 2.8 | 1.8 | 1.5 | 1.7 | 2.5 | 3.6 |
| Aromatic Hydrocarbons | NS | 57.7 | 62.7 | 64.5 | 66.7 | 65.6 | 60.9 |
| | S | 46.6 | 52.8 | 54.5 | 58.5 | 59.0 | 57.1 |
| Furans | NS | 0.6 | 1.0 | 0.9 | 0.8 | 0.6 | 0.4 |
| | S | 2.6 | 2.0 | 1.9 | 1.7 | 2.4 | 2.8 |
| Naphthenes | NS | 9.3 | 6.7 | 5.1 | 4.4 | 4.7 | 4.3 |
| | S | 6.9 | 5.8 | 5.5 | 5.6 | 4.2 | 4.5 |
| Phenols | NS | 10.1 | 10.0 | 9.7 | 8.2 | 8.4 | 7.7 |
| | S | 14.8 | 13.6 | 13.4 | 11.3 | 12.6 | 13.5 |
| Unidentified Fraction | NS | 12.0 | 11.1 | 9.9 | 9.5 | 11.5 | 16.4 |
| | S | 14.8 | 13.6 | 13.4 | 11.3 | 12.6 | 13.5 |
| Total | NS | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | S | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

D.5 Major compounds identified in organic distillate after upgrading of wood-oil over HZSM-5 at various temperatures.

| Temperature, °C | 290 | 330 | 350 | 370 | 390 | 410 |
|--|-----|-----|-----|-----|-----|-----|
| <u>Alcohols</u> | | | | | | |
| Cyclohexaneethanol ,-beta, 4- dimethyl-, trans | --- | 1.2 | 1.7 | 2.1 | 1.1 | 1.1 |
| <u>Aldehydes & Ketones</u> | | | | | | |
| Cyclooctanone, 2- methyl- | 1.3 | --- | --- | --- | --- | --- |
| 2-Cyclopentene-1- one, 2,3,4- trimethyl- | 2.5 | 1.3 | 0.9 | --- | --- | --- |
| <u>Phenols</u> | | | | | | |
| Phenol | --- | 1.9 | 1.3 | 1.6 | 1.2 | 1.1 |
| Phenol, 2-methyl- | 1.0 | --- | 1.1 | 1.2 | 0.9 | 0.9 |
| Phenol, 3-methyl- | --- | 2.1 | 2.0 | 1.8 | 0.3 | 0.3 |
| Phenol, 2,6- dimethyl- | 2.6 | 2.4 | 1.6 | 1.8 | 2.3 | 2.0 |
| Phenol, 2,3- dimethyl- | 2.6 | 2.4 | 1.6 | 1.8 | 2.4 | 2.0 |
| <u>Non-cyclic Aliphatic hydrocarbons</u> | | | | | | |
| Hexane | --- | --- | 0.9 | 0.7 | 0.4 | 0.2 |
| 1,4-Heptadiene, 3- methyl | --- | --- | 0.4 | 0.3 | 0.3 | --- |
| 3-Nonen-5-yne, 4- ethyl-, (E) | 2.2 | 1.5 | 1.4 | 1.7 | 2.9 | 1.5 |

Appendix D.5 continued.

| Temperature, °C | 290 | 330 | 350 | 370 | 390 | 410 |
|---|-----|------|------|------|------|------|
| <u>Cyclic Aliphatic Hydrocarbons</u> | | | | | | |
| Cyclopentane, 1-methyl-2-methylene- | 0.5 | 1.4 | 0.9 | 0.9 | 0.8 | 0.8 |
| Cyclohexane, 1-methyl-3-(1-methylethyl)-cis | 2.0 | 3.4 | 2.3 | 2.2 | 2.7 | 2.2 |
| Bicyclo[3.1.1]heptane dimethyl-3-methylene- | 3.4 | 0.9 | 0.3 | 0.3 | 0.3 | --- |
| <u>Aromatic Hydrocarbons</u> | | | | | | |
| Benzene | 2.5 | 6.6 | 6.8 | 10.2 | 11.6 | 8.0 |
| Benzene, methyl- | 9.8 | 13.1 | 16.2 | 15.2 | 14.6 | 17.4 |
| Benzene, ethyl- | 0.8 | 4.6 | 5.7 | 5.9 | 0.3 | 0.3 |
| Benzene, 1,4-dimethyl- | 4.7 | 14.4 | 16.0 | 15.0 | 13.1 | 13.0 |
| Benzene, 1,2-dimethyl- | 0.7 | 2.6 | 3.3 | 3.2 | 6.8 | 0.9 |
| Benzene, 1-ethenyl-2-methyl- | 2.8 | 0.0 | 3.5 | --- | --- | --- |
| Benzene, 1-propenyl- | 1.9 | 1.2 | 0.2 | 0.3 | 0.1 | 0.2 |
| Benzene, (2-methyl-2-propenyl)- | 3.4 | 0.8 | 2.3 | 1.9 | 3.0 | 0.0 |
| Benzene, 1-ethenyl-4-ethyl- | 1.1 | 1.0 | 1.5 | 1.4 | 1.6 | 1.4 |
| Naphthalene, decahydro- | 2.1 | 0.5 | 1.3 | 1.1 | 1.1 | 0.6 |
| Benzene, (1-methyl-2-cyclopropen-1-yl) | 2.1 | 2.7 | 1.6 | 1.5 | 1.1 | 0.8 |
| Benzene, (2-methyl-1-methylene propyl)- | 3.1 | 5.8 | 3.4 | 4.3 | 4.7 | 5.6 |

D.6 Effect of temperature on the yield of major hydrocarbon compounds identified in organic distillate obtained from upgrading wood-oil volatiles.

| Compound | Temperature, °C | | |
|---------------------------|-----------------|------|------|
| | 330 | 370 | 410 |
| Hexane | 1.2 | 0.7 | 0.6 |
| Benzene | 1.7 | 4.0 | 5.0 |
| Benzene, methyl- | 8.3 | 14.5 | 10.5 |
| Benzene, ethyl- | 2.7 | 4.6 | 4.0 |
| P-xylene | 10.5 | 13.6 | 8.4 |
| M-xylene | 1.8 | 3.1 | 2.0 |
| Benzene, 1,2,4-trimethyl- | 2.6 | 3.0 | 0.3 |
| Benzene, 1,2,3-trimethyl- | 3.2 | 1.8 | 0.6 |
| Benzene, (1-methylethyl)- | 2.1 | 3.4 | 1.4 |
| 1H-Indene | 0.6 | 0.7 | 0.9 |
| 1H-Indene, 1-ethylidene | 1.2 | 0.2 | 0.4 |

D.7 Effect of temperature on the yield of major hydrocarbons identified after upgrading over the catalysts.

| Catalyst | HZSM-5 | | | Silicalite | | | |
|--|-----------------|------|------|------------|-----|-----|-----|
| | Temperature, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| Compound | | | | | | | |
| Benzene | 1.7 | 3.2 | 3.7 | 0.6 | 2.8 | 2.7 | |
| Benzene, methyl- | 6.0 | 8.5 | 9.9 | 2.2 | 3.3 | 5.1 | |
| Benzene, ethyl- | 2.1 | 3.3 | 0.3 | 1.8 | 1.6 | 5.1 | |
| Xylenes (O+m+p) | 7.9 | 10.3 | 11.0 | 1.0 | 1.5 | 3.2 | |
| Benzene, 1-propenyl- | 0.5 | 0.5 | 0.1 | 0.1 | 0.6 | 0.5 | |
| Bicyclo[3.1.1]heptane dimethyl-3-methylene | 0.4 | 0.2 | --- | --- | --- | --- | |
| Benzene, (2-methyl-2-propenyl)- | 0.4 | 1.1 | --- | --- | --- | --- | |
| Benzene, 1-ethenyl-4-ethyl- | 0.5 | 0.8 | 0.8 | 2.1 | 2.0 | 1.9 | |
| 3-Nonen-5-yne, 4-ethyl-, [E]- | 0.7 | 1.0 | 0.9 | --- | --- | --- | |
| Benzene, (1-methyl-2-cyclopropen-1-yl)- | 1.3 | 0.9 | 0.6 | --- | --- | --- | |
| Benzene, (2-methyl-1-methylene propyl)- | 2.7 | 2.4 | 3.2 | --- | --- | --- | |

Appendix D.7 continued.

| Catalyst | H-Mordenite | | | H-Y | | | |
|--|-----------------|-----|-----|-----|-----|-----|-----|
| | Temperature, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| Compound | | | | | | | |
| Benzene | 0.2 | 0.4 | 0.4 | --- | --- | 0.3 | |
| Xylenes (O+m+p) | 0.4 | 1.3 | 0.2 | --- | 0.5 | 1.5 | |
| Benzene, 1,2,3-trimethyl- | 0.2 | 1.2 | 1.2 | 1.2 | 1.9 | 0.2 | |
| Benzene, 1,2,3,5-tetramethyl- | --- | 2.6 | 2.4 | 1.6 | 2.0 | 3.5 | |
| 3-Penten-1-yne | 1.2 | 1.5 | 0.8 | 1.0 | 0.9 | 0.5 | |
| 1,3,7-Octatriene, 3-7-dimethyl- | 0.8 | 1.3 | 0.7 | 0.3 | 0.8 | 0.6 | |
| Benzene, -ethenyl-2-methyl- | 1.5 | 0.1 | 1.4 | 1.6 | 2.6 | 3.2 | |
| 1H-Indene | 0.4 | 0.4 | 0.4 | 0.5 | 0.7 | --- | |
| 1H-Indene, 1-ethylidene | 3.7 | 4.6 | 4.1 | 0.7 | 0.8 | --- | |
| Benzene, (1,1-dimethyl-2-propenyl)- | 1.4 | 4.7 | 9.2 | 1.5 | 0.7 | --- | |
| 1H-Cyclopropane [B]Naphthalene, 1A, 2, 7, 7A-tetrahydro- | 0.8 | 0.9 | 0.8 | 1.1 | 0.4 | 4.2 | |
| 1H-Indene, 2,3-dihydro, 1,3-dimethyl- | 0.8 | 0.2 | 0.6 | --- | --- | --- | |

Appendix D.7 continued.

| Catalyst | Silica-alumina | | |
|---|----------------|-----|-----|
| | 330 | 370 | 410 |
| Temperature, °C | | | |
| Compound | | | |
| 1-Hexene | 0.9 | 2.0 | 3.9 |
| Pentane, 3-ethyl, 2,2-dimethyl- | --- | 0.5 | 0.9 |
| 1,4-Heptatriene, 3-methyl- | 0.7 | 0.3 | 0.2 |
| 1,3,5-Cycloheptatriene | 0.2 | 0.7 | --- |
| 1,4-Hexadiene, 3-ethyl- | 0.2 | 1.6 | 1.5 |
| Xylene (O+m+p) | 0.3 | 0.5 | 3.4 |
| Benzene, 1-propenyl- | 0.1 | --- | --- |
| 3-Nonen-5-yne, 4-ethyl- | 0.4 | 1.5 | 0.9 |
| Benzene, (2-methyl-1-methylene propyl)- | 0.2 | 0.2 | 1.4 |
| Naphthalene, 1-methyl- | 0.5 | 1.6 | 3.6 |
| Naphthalene, 1,7-dimethyl- | 0.4 | 0.3 | 2.2 |

D.8 Conversions for methyl ester acetic acid, cyclopentanone, phenol and methoxybenzene (100% concentration) reactivity over HZSM-5 catalyst.

| Propanoic acid | | | |
|--------------------|-------|------|------|
| Concentration, wt% | 100.0 | | |
| Temperature, °C | 330 | 370 | 410 |
| Conversion | 73.1 | 97.1 | 99.3 |
| Cyclopentanone | | | |
| Concentration, wt% | 100.0 | | |
| Temperature, °C | 330 | 370 | 410 |
| Conversion | 49.8 | 91.6 | 96.7 |
| Phenol | | | |
| Concentration, wt% | 14.6 | | |
| Temperature, °C | 330 | 370 | 410 |
| Conversion | 5.1 | 9.3 | 5.5 |
| Methoxybenzene | | | |
| Concentration, wt% | 100.0 | | |
| Temperature | 330 | 370 | 410 |
| Conversion | 39.1 | 72.4 | 66.9 |

Appendix E: COMPUTER PROGRAMS

Appendix E.1 Program for integration of product prediction models and solution of rate models.

This program solves a system of non-linear first order differential equations. It uses three IMSL library routines (SSET,UMACH and IVPRK). The procedure for compiling is as follows:

```

FOR NLRG.FOR
LINK NLRG, S_IFACE/LIBRARY,IMSL/LIBRARY
RUN NLRG
*****
INTEGER MXPARM,NEQ
PARAMETER (MXPARM=50,NEQ=2
INTEGER IDO,ISTEP,NOUT
REAL FCN,FLOAT,PARAM(MXPARM),T,TEND,TOL,Y(NEQ)
INTRINSIC FLOAT
EXTERNAL FCN,IVPRK,SSET,UMACH
CALL UMACH (2,NOUT)
**** SET INITIAL CONDITIONS ****
Y(1)=0.0
Y(2)=0.0
**** SET ERROR TOLERANCE
TOL=0.0005
**** SET PARAM TO DEFAULT ****
CALL SSET (MXPARM,0.0,PARAM,1)
**** SELECT ABSOLUTE ERROR CONTROL ****
PARAM(10)=1.0
**** PRINTER HEADER ****
WRITE (*,111)
111 FORMAT (4X,'ISTEP',5X,'TIME',9X,'Y1',9X,'Y2')
IDO=1
DO 10 ISTEP=1,10
TEND=FLOAT(ISTEP)
CAL IVPRK(IDO,NEQ,FCN,T,TEND,TOL,PARAM,Y)
WRITE(*,'(I6,5F12.5)') ISTEP,T,Y
10 CONTINUE
IDO=3
CALL IVPRK (IDO,NEQ,FCN,T,TEND,TOL,PARAM,Y)
STOP
END
**** SUBROUTINE ****
SUBROUTINE FCN(NEQ,T,Y,YPRIME)
INTEGER NEQ
REAL T,Y(NEQ),YPRIME(NEQ),K1,...KN,a1...aN
**** SET VALUES FOR RATE CONSTANTS, K1...kN, REACTION ORDERS,
**** r,cr,opl,a,g,c, AND WOOD-OIL CONCENTRATION, CW ****
IF(Y(2).LT.0.0)Y(2)=e-10
IF(Y(1).LT.0.0)Y(1)=e-10
YPRIME(1)=(K1*CW-K2*Y(1)**r-K4*Y(1)**c)
T1=K3*CW+K8*Y(1)**cr

```

```

T2=-K4*Y(2)**op1-K5*Y(2)**a
T3=-K6*Y(2)**g-K7*Y(2)**c
YPRIME(2)=T1+T2+T3
RETURN
END

```

E.2 Program for Parameter Estimation.

This program performs a least square fit of input data to non-linear functions. This routine uses two IMSL library routines (U4LSF and UNLSF). The procedure for compiling is as follows:

```

FOR NLRG.FOR
LINK NLRG, S_IFACE/LIBRARY,IMSL/LIBRARY
RUN NLRG
*****
PARAMETER (IM=4,JM=2) ! IM IS THE NUMBER OF DATA POINTS.
EXTERNAL FCN,UNLSF,U4LSF !JM IS THE NUMBER OF CONSTANTS

INTEGER LDFJAC,M,N,Q
INTEGER IPARAM(6) ! X() IS FOR UNKNOWNNS
REAL X(JM),F(IM),FJAC(IM,JM),RPARAM(7),Y(IM),X1(IM),
REAL XGUESS(JM),XSCAL(JM),FSCALE(IM),FVEC(IM)
1 !X1()... ARE THE DATA
COMMON Y,X1 ! INPUT VECTORS WITH Y()
CHARACTER*13 AFILE,GFILE

**** INITIALIZATION SECTION ****
OPEN(UNIT=21,FILE='JAC.DAT',ACCESS='SEQUENTIAL',STATUS=
1 'NEW)
N=JM
LDFJAC=IM
DO 3 I=1,IM
FSCALE(I)=1.0
3 CONTINUE
DO 4 I=1,N
XSCALE(I)=1.0
4 CONTINUE
TYPE *, ' INPUT INITIAL GUESSES FILE'
ACCEPT 100, GFILE
100 FORMAT(A13)
OPEN(UNIT=2,FILE=GFILE,STATUS='OLD')
READ(2,*)(XGUESS(I),I=1,JM)
CLOSE(UNIT=2,STATUS='SAVE')
TYPE *, ' INPUT NAME OF FILE FOR X AND Y DATA'
ACCEPT 100, AFILE
OPEN(UNIT=1,FILE=AFILE,STATUS='OLD')
READ(1,*) M
DO 10 I=1,M
READ(1,*)XI(I),Y(I)
10 CONTINUE

```

```

IPARAM(1)=1.0
CALL U4LSF(IPARAM, RPARAM)
CALL UNLSF(FCN, M, N, XGUESS, SCALE, FSCALE, IPARAM, RPARAM, X,
1      FVEC, FJAC, LDFJAC)
SSQ=SDOT(M, FVEC, 1, FVEC, 1)**2
**** RESULTS ****
TYPE*, FVEC
TYPE*, 'THE UNKOWN CONSTANTS ARE:'
TYPE 101, ((I, X(I), I=1, N
101  FORMAT('BETA(', I2, ')='e15.8)
TYPE *, 'THE NUMBER OF ITERATIONS IS: ', IPARAM(4)
TYPE *, 'THE NUMBER OF FUNCTION EVALUATIONS IS: ', IPARAM(4)
TYPE *, 'LEAST SQUIRES ERROR=', SSQ
DO 102 J=1, M
102  CONTINUE
TY=, 0.0
TT=0.0
DO 11 I=1, M
TREM=ABS(FVEC(I))
TY=TY+FVEC(I))
11  TT=TT+TREM
TT=TT/M*100
TY=TY/M*100
TYPE *, TT, TY
STOP
END
**** SUBROUTINE ****
SUBROUTINE FCN(M, N, X, F)
PARAMETER(IM=4, JM=2)
DIMENSION F(IM), Y(IM), X1(IM), X(JM)
COMMON Y, X1,
DO 103 I=1, M
F(I)=X(1)*X1(I)**X(2)
103  CONTINUE
RETURN
END

```

Appendix F: RESULTS FROM KINETIC MODELLING

F.1 Sample calculation: Evaluation of Rate-concentration data, parameter estimations and product prediction (concentrations) from models.

Sample calculations for rate-concentration data

| Product | Molecular Weight (Average) |
|---------------------------|-------------------------------|
| Aqueous Fraction | 18 |
| Coke | 12 |
| Gas | 45 |
| Residue | 350 |
| Hydrocarbon-rich Fraction | 87 |
| Wood-oil Volatiles | 85 |
| Hydrocarbons | 87 |

Sample calculation: at 330 °C, 30.9 feed concentration (Wood-oil Volatiles), for organic distillate.

Feed rate = 2.5 g per 30 min process time.
= 5.8×10^{-5} Kmol/h

Yield of OLP = 2.3 g

Conversion to OLP = 92 %

Mass of catalyst = 0.002 Kg

Volume of reactor = 9.5×10^{-7} m³

Concentration = (mass (Kg)+mol. weight)/Volume of reactor(m³)
= $(0.0023/87)/9.5 \times 10^{-7}$
= 27.8 Kmol/m³

Rate = $F/W (X_{out} - X_{in})$
= $(5 \times 10^{-5}/0.002) (0.92-0.0)$
= 266.6×10^{-4} Kmol/Kcat. h.

Rate-concentration data were calculated for each product at all concentrations and temperatures following the same format.

Application of program for parameter estimations provides estimates of the kinetic parameters.

F.2 Results from kinetic modeling.

Reactivity data for non-volatile formation path.

| | | | |
|---|------|-----|-----|
| Feed Concentration K mole/m ³ | 10.3 | | |
| Temperature, °C | 330 | 370 | 410 |
| Product Concentration, K mole/m ³ | 5.2 | 4.5 | 2.8 |
| Reaction Order | 1.0 | 1.0 | 1.0 |
| Rate Constant | 0.5 | 0.4 | 0.3 |

Activation Energy, (KJ/Kmol) = -2.5×10^4

Reactivity data for volatiles formation path.

| | | | |
|---|------|------|------|
| Feed Concentration K mole/m ³ | 10.3 | | |
| Temperature, °C | 330 | 370 | 410 |
| Product Concentration, K mole/m ³ | 9.1 | 11.7 | 19.0 |
| Reaction Order | 1.0 | 1.0 | 1.0 |
| Rate Constant | 0.9 | 1.1 | .8 |

Activation Energy, (KJ/Kmol) = 3.0×10^4

Reactivity data for aqueous formation path.

| | | | | | | |
|--|----------------|-----|-----|------------------------|-----|-----|
| Feed Concentration K mole/m ³ | 30.9 | | | 13.6 | | |
| Temperature, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| Product Concentration, K mole/m ³ | 0.8 | 3.3 | 3.6 | 0.2 | 0.9 | 2.0 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | 1.5 | 6.4 | 7.2 | 0.4 | 1.9 | 4.0 |
| Feed Concentration, K mol/m ³ | 7.7 | | | 3.2 | | |
| Product Concentration, K mol/m ³ | 0.1 | 0.4 | 0.5 | 0.1 | 0.1 | 0.2 |
| Rate of Formation x 10 ⁴ , K mol/Kgcat.h | 0.2 | 0.7 | 1.1 | 0.1 | 0.3 | 0.1 |
| Temperature, °C | Reaction Order | | | Rate Constant | | |
| 330 | 1.5 | | | 1.0 x 10 ⁻⁶ | | |
| 370 | 1.6 | | | 3.4 x 10 ⁻⁶ | | |
| 410 | 1.4 | | | 6.1 x 10 ⁻⁶ | | |
| Activation Energy, (KJ/Kmol) = 7.6 x 10 ⁴ | | | | | | |
| Preexponential Factor, = 1.45 | | | | | | |

Reactivity data for coke formation paths.

| Feed Concentration K mole/m ³ | | 30.9 | | | 13.6 | | |
|---|----------------|------|------|------------------------------------|------|------|------|
| Temperature, °C | | 330 | 370 | 410 | 330 | 370 | 410 |
| Product Concentration , K mole/m ³ | V | 6.9 | 17.5 | 35.3 | 1.9 | 6.3 | 9.3 |
| | NV | 7.9 | 20.4 | 40.9 | 2.8 | 10.6 | 16.5 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | V | 9.3 | 23.2 | 46.7 | 2.6 | 8.3 | 12.5 |
| | NV | 2.4 | 6.5 | 13.1 | 0.9 | 3.4 | 5.3 |
| Feed Concentration , K mol/m ³ | | 7.7 | | | 3.2 | | |
| Product Concentration , K mol/m ³ | V | 1.1 | 3.6 | 5.4 | 0.5 | 1.7 | 2.2 |
| | NV | 2.2 | 5.3 | 7.5 | 0.9 | 3.1 | 4.0 |
| Rate of Formation x 10 ⁴ , K mol/Kgcat.h | V | 1.5 | 4.7 | 7.2 | 0.6 | 2.3 | 3.1 |
| | NV | 0.7 | 1.7 | 2.4 | 0.3 | 1.0 | 1.3 |
| Temperature, °C | Reaction Order | | | Rate Constant x 10 ⁵ | | | |
| | V | NV | | V | NV | | |
| 330 | 1.2 | 0.9 | | 1.4 | 1.0 | | |
| 370 | 1.1 | 0.9 | | 6.4 | 3.4 | | |
| 410 | 1.2 | 1.1 | | 7.5 | 3.7 | | |
| Activation Energy, (KJ/Kmol): V = 7.3 x 10 ⁴ NV = 4.9 x 10 ⁴ | | | | | | | |
| Preexponential Factor: ¹ V = 33.1 ² NV = 0.2 | | | | | | | |

¹ Volatiles² Non-volatiles

Reactivity data for gas formation path.

| | | | | | | |
|--|----------------|------|------|------------------------|-----|------|
| Feed Concentration K mole/m ³ | 30.9 | | | 13.6 | | |
| Temperature, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| Product Concentration, K mole/m ³ | 1.2 | 2.7 | 5.5 | 1.1 | 1.8 | 2.5 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | 6.1 | 13.6 | 27.3 | 5.3 | 8.8 | 12.6 |
| Feed Concentration, K mole/m ³ | 7.7 | | | 3.2 | | |
| Product Concentration, K mole/m ³ | 0.6 | 1.0 | 1.8 | 0.5 | 0.5 | 0.8 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | 3.1 | 5.0 | 9.1 | 2.6 | 2.6 | 4.1 |
| Temperature, °C | Reaction Order | | | Rate Constant | | |
| 330 | 0.7 | | | 0.7 x 10 ⁻⁴ | | |
| 370 | 0.7 | | | 1.1 x 10 ⁻⁴ | | |
| 410 | 0.8 | | | 1.8 x 10 ⁻⁴ | | |
| Activation Energy, (KJ/Kmol) = 3.7 x 10 ⁴ | | | | | | |
| Preexponential Factor, = 0.12 | | | | | | |

Reactivity data for organic distillate formation path.

| | | | | | | |
|--|----------------|-------|-------|------------------------|-------|------|
| Feed Concentration K mole/m ³ | 30.9 | | | 13.6 | | |
| Temperature, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| Product Concentration, K mole/m ³ | 27.8 | 24.2 | 19.2 | 12.4 | 10.9 | 9.7 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | 266.6 | 232.0 | 184.6 | 120.1 | 105.5 | 93.5 |
| Feed Concentration, K mole/m ³ | 7.7 | | | 3.2 | | |
| Product Concentration, K mole/m ³ | 7.1 | 6.4 | 5.5 | 2.7 | 2.5 | 2.2 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | 67.7 | 61.0 | 52.9 | 26.5 | 24.7 | 21.9 |
| Temperature, °C | Reaction Order | | | Rate Constant | | |
| 330 | 1.0 | | | 8.6 x 10 ⁻⁴ | | |
| 370 | 1.0 | | | 8.3 x 10 ⁻⁴ | | |
| 410 | 0.9 | | | 8.0 x 10 ⁻⁴ | | |
| Activation Energy (KJ/Kmol), = 2.9 x 10 ³ | | | | | | |
| Preexponential Factor, = 4.9 x 10 ⁻⁴ | | | | | | |

Reactivity data for hydrocarbon formation path.

| | | | | | | |
|--|----------------|-------|------|------------------------|------|------|
| Feed Concentration K mole/m ³ | 30.9 | | | 13.6 | | |
| Temperature, °C | 330 | 370 | 410 | 330 | 370 | 410 |
| Product Concentration, K mole/m ³ | 11.9 | 13.7 | 10.3 | 6.3 | 7.0 | 7.0 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | 114.3 | 131.4 | 98.6 | 61.4 | 67.9 | 68.4 |
| Feed Concentration, K mol/m ³ | 7.7 | | | 3.2 | | |
| Product Concentration, K mol/m ³ | 3.8 | 4.4 | 4.0 | 1.5 | 1.7 | 1.7 |
| Rate of Formation x 10 ⁴ , K mol/Kgcat.h | 36.9 | 41.8 | 38.5 | 15.4 | 17.3 | 16.6 |
| Temperature, °C | Reaction Order | | | Rate Constant | | |
| 330 | 0.9 | | | 5.8 x 10 ⁻⁴ | | |
| 370 | 0.9 | | | 6.0 x 10 ⁻⁴ | | |
| 410 | 0.8 | | | 6.8 x 10 ⁻⁴ | | |
| Activation Energy, (KJ/Kmol) = 6.7 x 10 ³ | | | | | | |
| Preexponential Factor, = 2.1 x 10 ⁻³ | | | | | | |

Reactivity data for cracking path.

| Feed Concentration K mole/m ³ | 10.3 | | | 4.5 | | |
|--|----------------|-----|-----|------------------------|-----|-----|
| | 330 | 370 | 410 | 330 | 370 | 410 |
| Product Concentration, K mole/m ³ | 1.8 | 2.5 | 1.3 | 0.9 | 1.2 | 0.7 |
| Rate of Formation x 10 ⁴ , K mole/Kgcat.h | 4.3 | 5.8 | 3.0 | 2.0 | 2.7 | 1.6 |
| Feed Concentration, K mol/m ³ | 2.6 | | | 1.1 | | |
| Product Concentration, K mol/m ³ | 0.5 | 0.8 | 0.4 | 0.2 | 0.3 | 0.2 |
| Rate of Formation x 10 ⁴ , K mol/Kgcat.h | 1.2 | 1.8 | 1.0 | 0.5 | 0.7 | 0.4 |
| Temperature, °C | Reaction Order | | | Rate Constant | | |
| 330 | 0.9 | | | 4.9 x 10 ⁻⁵ | | |
| 370 | 0.9 | | | 6.8 x 10 ⁻⁵ | | |
| 410 | 0.9 | | | 4.1 x 10 ⁻⁵ | | |
| Activation Energy (KJ/Kmol), = 2.4 x 10 ⁴ | | | | | | |
| Preexponential Factor, = 6.1 x 10 ⁻³ | | | | | | |

