**University of Alberta**

# Free Radical Chain Mechanism for Bitumen Conversion

by

Carolyn Ann Blanchard ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment

of the requirements for the degree of Master of Science

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Friday, July 19, 1996

**To Mom and Jeff,**
**Thanks**

# Abstract

The role of free radical chain reactions in cracking of the residue fraction of Athabasca bitumen was explored by conducting experiments in a batch reactor at 400°C. Bitumen was diluted with 1-methyl naphthalene and cracked under hydrogen at 13.8 MPa for 1 h. The conversion of bitumen was reduced, relative to control experiments without diluent, and the yield of termination products from the solvent was increased by 5.9 fold. The suppression of conversion due to adding a solvent was variable from experiment to experiment, possibly due the D-1160 distillation analysis.

Addition of ethylene altered the residue characteristics, giving an increase in the aromatic carbon region and an increase in coke yield. These changes were consistent with reactions between the ethylene and the bitumen radicals. Dilution of the residue may also suppress coke formation under a nitrogen atmosphere, but further studies are required.

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## List of Abbreviations

| | |
|---|---|
| CCR | Conradson carbon residue |
| ESR | electron spin resonance |
| F-S-S | Fabuss-Smith-Satterfield |
| GC | gas chromatograph |
| GC-MS | gas chromatograph - mass spectrometry |
| H/C | hydrogen / carbon |
| 1-MN | 1-methyl naphthalene |
| NMR | nuclear magnetic resonance |
| PAH | polynuclear aromatic hydrocarbons |
| RHT | radical hydrogen transfer |
| SANS | small angle neutron scattering |
| TLP | total liquid products |

# 1.0 Introduction

As the supply of conventional crude oil diminishes, more importance is being placed on upgrading of heavier oils, such as bitumen. One of the main components of bitumen is residue, the fraction of petroleum, heavy oil or bitumen that does not distill under vacuum and has a boiling point over 524°C (Gray, 1994). Residues are a complex mixture of many components with high sulfur and metal content, low H/C ratio and high molecular weight. Upgrading the residue reduces the molecular weight to produce distillate products. Depending on the process, a variety of other reactions could also occur. The complexity of residues has prevented the development of mechanistic models for the reactions that occur during upgrading. The focus throughout this thesis will be the conversion of residue by cracking to reduce molecular weight.

The purpose of this investigation was to determine the mechanism of conversion of the residue fraction of Athabasca bitumen and to probe the nature of radicals. Cracking of hydrocarbons in the gas phase proceeds via a free radical chain mechanism. Previous work by Khorasheh and Gray (1993) in the liquid phase showed that the same mechanism was responsible for cracking model compounds at high pressure in the presence of a solvent. From this work it was proposed that cracking of bitumen residue proceeds by a conventional free radical chain reaction.

The role of free radical chain reactions was tested by adding 1-methyl naphthalene as an alternate radical carrier to the residue undergoing thermal cracking. The expected result was that the 1-methyl naphthalene would compete with the bitumen molecules in radical transfer reactions and thereby reduce the residue conversion. The experimental variables of interest were the change in residue conversion and the yield of 1-methyl naphthalene derived termination products.

The second set of experiments was designed to probe for radicals by the addition of an alkene (in this case ethylene). Addition of ethylene to radicals in the residue fraction would result in addition of aliphatic chains to residue radicals. These added aliphatic groups could be measured by NMR spectrometry to provide insight into the radicals formed during residue upgrading.

One of the major problems in upgrading is the formation of coke, a solid carbonaceous material. If coking also proceeds by a free radical chain mechanism, then adding an alternate radical carrier would suppress coke formation. By diluting the residue with 1-methyl naphthalene and cracking it under a nitrogen atmosphere, the bimolecular reactions important during coking would be suppressed. In the absence of such a solvent, coke would form. The indications that coke formation was suppressed would be an increase in 1-methyl naphthalene derived termination products as compared to pure solvent and a decrease in solids formation as compared to undiluted residue reacted under the same conditions.

Reactions were performed in a 500 mL batch reactor in the absence of an added catalyst. All experiments were performed at a temperature of 400°C and pressures of 13.8 MPa (for diluent experiments with hydrogen) or 10.7 MPa (for ethylene and coking experiments) to investigate the hypotheses. The reactant was Athabasca bitumen with a boiling point over 424°C.

# 2.0 Literature Review

## 2.1 Upgrading of Petroleum and Bitumen Residues

Upgrading of residue fractions from petroleum, heavy oil and bitumen is becoming a more important refinery process due to the decreasing supply of conventional oil with a low residue content. The feasibility of upgrading these heavy fractions is influenced by two main factors. The first is the cost of processing residue to synthetic crude oil and the second is the feasibility of shipping the products to consumers (Schuetze and Hofmann, 1984). Undiluted residues are difficult to transport because of their high viscosities and cannot be used as a sole feedstock to a refinery because of their high metals content and high sulfur content.

Residues are composed of high molecular weight compounds, consisting mainly of resins and asphaltenes (Le Page et al., 1987) which are large molecules composed of hydrogen, carbon, nitrogen, sulfur and oxygen (Ebert et al., 1987). Residues have high viscosities, high sulfur and metal contents, and low H/C ratio as compared to distillate fractions in crude oil (Schuetze and Hofmann, 1984). Table 2.1 gives a comparison between the properties of a representative crude oil and a residue.

Table 2.1: Comparison of Crude Oil and Residue Properties

| Properties | Light Crude | Athabasca Vacuum Residue |
|---|---|---|
| API Gravity | 38 | 2.1 |
| Sulfur, wt % | 0.5 | 6.18 |
| Metals, ppm | 22 | 490 |

(Data from Dolbear et al., 1987 and Wenzel, 1992)

### 2.1.1 Residue Conversion

There are two main goals in upgrading residue: to convert the 524°C+ fraction to distillable liquids and to improve product quality by removing sulfur and metals (Beaton and Bertolacini, 1991). The two main groups of processes used for upgrading residues are hydrogenation processes and non-hydrogenation processes (with or without hydrogen). These can further be subdivided into catalytic and non-catalytic processes. Table 2.2 indicates some of the most common processes available under each category. The optimal choice of a process depends on the properties of residue, the product desired and the overall economics (Heck et al., 1992).

Table 2.2: Residue Processing Options

| **Hydrogenation Processes** | | **Non-hydrogenation Processes** | |
|---|---|---|---|
| Catalytic | Non-Catalytic | Catalytic | Non-Catalytic |
| LC-fining | Hydrovisbreaking | Fluid Catalytic Cracking | Visbreaking |
| ABC | Donor-solvent | | Delayed Coking |
| H-Oil | Hydropyrolysis | | Fluid Coking |

Hydrogenation processes have some advantages over other upgrading processes. The addition of hydrogen results in volume expansion in the liquid phase, giving a larger volumetric yield. Hydrogen also helps to reduce the amount of coke, a high carbon-content solid that fouls equipment (Beaton and Bertolacini, 1991). At high pressures, hydrogen can act as a diluent to inhibit bimolecular addition or condensation reactions (Bunger, 1985). Addition of hydrogen also enhances the hydrogen abstraction reactions by alkyl radicals (Khorasheh and Gray, 1994). Offsetting the benefits of hydrogen are its cost and the increased expense for high pressure operation. Hydrogenation processes are usually favored over non-hydrogenation processes if little or no coke is desired as an ultimate product.

In contrast, if coke is desired, non-hydrogenation processes are used without adding a catalyst. In the absence of a high partial pressure of hydrogen, these processes produce a large quantity of coke (Schuetze and Hofmann, 1984). The yield of distillate products from coking processes is lower than in hydrogenation because one of the significant products is solid coke (Schuetze and Hofmann, 1984). The one advantage of coking processes, however, is that the residue present in the feed is virtually eliminated (Gray, 1994).

The chemistry of coke formation is complex and may involve both chemical reactions and thermodynamic phase properties (Gray, 1994). The chemical reactions leading to coke formation are bimolecular condensation reactions, forming aromatic components with high molecular weights and bridging them together. Coke formation may also be linked to colloidal properties of the asphaltenes in the residue, since this soluble fraction is often suggested as the source of coke precursors (Gray, 1994). Since coke ultimately forms as a new phase, the phase behavior at reaction conditions may affect the ultimate yield.

Upgrading of residues usually begins with the thermal breaking of bonds (Heck et al., 1992). Research has indicated that even though the addition of hydrogen and catalysts can help convert residue, the reaction is primarily thermally driven (Schuetze and Hofmann, 1984; Heck and DiGuiseppi, 1993). The various processes for upgrading, therefore, vary mainly in how the initial products from thermal cracking are directed through secondary reactions, and how coke formation is either controlled or directed.

Residue conversion has been shown to depend on several factors. Heck et al. (1992) found that product yield during residue conversion is a function of thermal severity, or equivalent residence time at 427°C. Heck and DiGuiseppi (1993) also found that to increase the thermal severity, higher reaction temperatures and longer residence times should be used. Residue conversion is not strongly affected by catalyst activity in the hydrogenation processes and hence thermal reactions can be decoupled from catalytic reactions (Beaton and Bertolacini, 1991). Although the empirical behavior of residues is established through process operating experience, the details of the underlying chemistry are poorly understood.

### 2.1.2 Chemistry of Residue Conversion

Strausz (1989) has indicated that two factors govern the chemical behavior of the residue during upgrading: the molecular structure and the molecular size distribution. A highly aromatic structure is believed to be less reactive. The reactivity depends on the aliphatic bonds only, because aromatic rings are too stable to crack. Therefore the nature of substituents on aromatic rings, length of side chains, and size of condensed naphthenic rings will all effect the reactivity. Reactivity may change as conversion continues because the balance between these groups may shift (Nagaishi et al., 1995).

The complex nature of the residue makes it difficult to determine the exact mechanism for residue conversion. A number of authors have pointed out that cracking of residue must involve the removal of largely aliphatic fragments from a more aromatic core including Savage and Klein (1985), Heck and DiGuiseppi (1993), Gray (1994), Wiehe (1993), and Sanford (1994). The mechanism of how this decomposition occurs in heavy hydrocarbons has not been proven. In pyrolysis of light hydrocarbons at low pressure, the work of Kossiakoff and Rice (1943) demonstrated the importance of free radical chain reactions. Free radicals are normally thought to be the active intermediates in residue cracking, but the mechanisms of their reactions are poorly defined.

## 2.2 Free Radical Chain Reactions

A radical is defined as an atomic or molecular species having an unpaired electron. Early chemists where skeptical that radicals existed but experiments performed by Moses Gomberg in 1900 indicated that radicals do exist. The radicals observed during the reactions were eventually termed free radicals and were shown to be active intermediates during chemical reactions (Reusch, 1977). Free radicals can react with an adjacent molecule, decompose into a stable compound and a smaller radical or diffuse to the wall and be absorbed there (Rice, 1931).

In the early 1930's much work was performed to define how aliphatic hydrocarbons decompose in the gas phase. Rice (1931) examined the gas-phase decomposition of n-alkanes from methane through to pentane. Each reaction was described by a free radical mechanism with the following simplifying assumptions. Low conversions were used to ensure only the original substance reacted and only methyl and ethyl groups were considered to be stable radicals. An example of the mechanism developed for ethane based on these assumptions is depicted below.

Initiation:

$$CH_3CH_3 \longrightarrow 2CH_3^{\bullet} \qquad (1)$$

Propagation:

$$CH_3CH_3 + CH_3^\bullet \longrightarrow CH_4 + CH_3CH_2^\bullet \qquad (2)$$

$$CH_3CH_2^\bullet \longrightarrow CH_2{=}CH_2 + H^\bullet \qquad (3)$$

$$CH_3CH_3 + H^\bullet \longrightarrow H_2 + CH_3CH_2^\bullet \qquad (4)$$

Rice and Herzfeld extended the above theory to include more complex hydrocarbons by assuming that decomposition reactions of alkyl radicals are faster than bimolecular reactions with other hydrocarbons (Rice and Herzfeld, 1934), and that the initial formation of a radical depends on the relative ease of abstraction of H-atom from a hydrocarbon (Kossiakoff and Rice, 1943). Free radicals with a carbon chain of six carbons or higher can also isomerize by a coiling mechanism to a carbon atom four or more carbon atoms from the carbon atom having the unpaired electron (i.e. if the alkane is long enough it can bend around and react with itself; Rice and Herzfeld, 1934). Long chain radicals can coil around and react with themselves to form an isomer ( Kossiakoff and Rice, 1943). The general mechanism arising from the work by Rice and Herzfeld is depicted below.

Initiation:

$$M \longrightarrow R_i^\bullet + R_j^\bullet \qquad (5)$$

Hydrogen Transfer:

$$R_1^\bullet + M \longrightarrow R_1H + M^\bullet \qquad (6)$$

β-scission:

$$M^\bullet \longrightarrow n\text{-}R_2^\bullet + \text{Olefin} \qquad (7)$$

$$R_i^\bullet \longrightarrow n\text{-}R_{i-2}^\bullet + CH_2{=}CH_2 \quad (i \geq 4) \qquad (8)$$

Isomerization:

$$R_p^\bullet \rightleftharpoons R_s^\bullet \qquad (9)$$

Termination:

$$R_i^\bullet + R_j^\bullet \longrightarrow \text{Products} \qquad (10)$$

Here M and M $^{\bullet}$ represent the parent alkane and the parent radical, $R_1^{\bullet}$ and $R_1H$ are the methyl or ethyl radical and the corresponding alkane, $R_2^{\bullet}$ is the methyl or ethyl or higher primary alkyl radical, $R_i^{\bullet}$ is a butyl or higher radical and finally $R_p^{\bullet}$ and $R_s^{\bullet}$ are primary and secondary pentyl or higher radicals.

These studies were all performed at low temperature and pressure, and in the gas-phase. Activation energies for the main reactions in free radical chain reactions are well defined for aliphatic compounds. Homolytic carbon-carbon bond cleavage (i.e. reaction (1)) has a high activation energy in the range of 213 - 398 kJ/mol (Billaud et al., 1988; Khorasheh and Gray, 1993; Sundaram and Froment, 1978). β-scission has an activation energy in the range of 125 - 146 kJ/mol (i.e. reaction (7) and (8)), and hydrogen abstraction has an activation energy in the range of 46 - 71 kJ/mol (i.e. reaction (6); Billaud et al., 1988; Khorasheh and Gray, 1993). The activation energies for these reactions show that hydrogen abstraction and β-scission are the preferred reactions and homolytic carbon-carbon bond cleavage has a much larger energy requirement. The repetition of many hydrogen abstraction and β-scission reactions for every radical formed by homolytic scission gives a chain reaction that overcomes the energy barrier of the initial step.

Rice (1931) employed two different tests to study the nature of chain reactions involving radicals. The first test was to prove the existence of carriers and other fragments (carriers are the radicals that continue chain reactions) by heating hydrocarbons in a rapid current of hydrogen in a long tube. If methyl groups were found to react further down the tube (i.e. 40 cm) then carriers were said to exist. The second test that Rice performed was to increase the surface area per unit volume and observe differences in species formed. If little difference was found than the chains were assumed to be terminated chiefly by collisions between alkyl radicals and not with the walls.

A more recent approach is through the use of electron spin resonance (ESR) spectroscopy. The resonance resulting from a magnetic moment produced by the spin of an unpaired electron gives an ESR spectra of many lines. These absorption lines are related to the magnetic quantum number of the nucleus of a free radical. Each unpaired electron produces different absorption lines depending on the species it was attached to. From the spectra produced, researchers could determine if free radicals existed in the reaction being studied. (Reusch, 1977; Perry et al., 1984)

ESR allows researchers to examine the radicals formed during reactions and to develop concise reaction steps. For example, Livingston et al. (1979) examined the role played by free radicals in high temperature reactions. They investigated the reactive intermediates found at steady state concentrations during the pyrolysis of bibenzyl (1,2-diphenylethane) in benzene. The ESR spectra revealed a 1,2-diphenylethyl radical and this observation was used to develop a detailed mechanism. ESR analysis of reaction systems has direct applications, therefore, in developing free radical mechanisms for pure compounds. In complex mixtures, such as residues, ESR can indicate the total radical concentration but is less useful in defining the chemical structure of the active species.

## 2.3 Empirical Studies on Complex Mixtures

The theory of free radical chain reactions was developed based on the behavior of pure hydrocarbons. Curran et al. (1967) first developed a free radical mechanism for complex mixtures in the conversion of coal to liquid products. The experiments were performed using a coal-tetralin slurry, to examine the transfer of hydrogen from tetralin to bituminous coal. They observed that the rate of hydrogen transfer was the same with various active donors (perhydrophenanthrene, decalin, indane and cyclohexane), and the rate of thermal decomposition of coal determined the extent of hydrogen transfer when a sufficiently reactive active donor was used. Curran et al. (1967) suggested the following mechanism for coal, assuming that at high tetralin concentrations the recombination of radicals and donation of hydrogen by coal molecules can be neglected:

$$M \longrightarrow 2\,R^{\bullet} \tag{11}$$

$$R^{\bullet} + Tet \longrightarrow RH + Tet^{\bullet} \tag{12}$$

$$Tet^{\bullet} \longrightarrow (Tet - H_2) + H^{\bullet} \tag{13}$$

$$H^{\bullet} + Tet \longrightarrow Tet^{\bullet} + H_2 \tag{14}$$

$$R^{\bullet} + Tet^{\bullet} \longrightarrow RH + (Tet - H_2) \tag{15}$$

Where M is the coal extract, $R^{\bullet}$ is a radical, Tet is tetralin, $Tet^{\bullet}$ is a radical produced by abstracting a hydrogen from the tetralin, and ($Tet - H_2$) is dihydronaphthalene derived from the tetralin (Curran et al., 1967). Dihydronaphthalene would react further, donating hydrogen to radicals and forming naphthalene. The overall reaction suggested by the mechanism was that each mole of hydrogen transferred was coupled with the dissociation of a carbon-carbon bond into two radicals.

From the above mechanism, cracking of coal in the presence of tetralin should have formed molecular hydrogen ($H_2$). Curran et al. (1967) found small values for activation energies (125.5 kJ/mol and 188.3 kJ/mol) relative to bond dissociation energies.

They estimated entropies of reaction using the theory of absolute reactions by Glasstone et al. (1941), and found negative values. Entropies are usually positive for unimolecular reactions where dissociation into free radicals occurs (Benson, 1976). It is unlikely that the values calculated by Curran truly represent the energies associated with the chemical reactions of coal since it is difficult to evaluate the energies of the transition states of a complex mixture.

Neavel (1976) investigated the liquefaction of coal in hydrogen donor and non-donor solvents and proposed a free radical mechanism. He observed that oxidation helped the liquefaction process and postulated that the oxygen-coal bonds cracked readily to form free radicals, thus consuming donor hydrogen or permitting repolymerization when a donor was unavailable. Neavel's mechanism was a rather simplified form of Curran et al (1967) with hydrogen being abstracted from the donor solvent to stabilize the free radicals formed by pyrolysis.

The use of non-donor solvents, such as naphthalene and dodecane, gave a decrease in the yield of benzene-soluble material i.e. a lower yield of low-molecular weight products. Neavel postulated that the free radicals reacted with surrounding molecules to give a net increase in the molecular weight, so that the overall yield of liquids in prolonged reaction of hydrogen-donor deficient mixtures would be significantly lower than in tetralin rich systems. The experiments with tetralin showed that the reaction rate in the later stages of reaction was independent of the donor hydrogen concentration. This observation seems to contradict the model of Neavel (1976) and Curran et al. (1967) since the model states that radicals are stabilized by hydrogen which was abstracted from the solvent. The rate of reaction (12) should depend on the solvent concentration. This trend was observed by Curran et al. (1967). The other main observation was that hydrogen from the tetralin was consumed in the conversion of coal, giving the dehydrogenated products dihydronaphthalene and naphthalene.

The above two free radical mechanisms of Curran et al. (1967) and Neavel (1976) were developed from observation of coal processing, but the same concepts have been applied to petroleum residues and bitumen. In a recent example, Sanford and Chung (1991) investigated pitch conversion and developed a similar free radical mechanism to describe the experimental results. They observed that the presence of hydrogen or an H-donor solvent suppressed coke formation and that little gas or reactor solids formed for the first 30% conversion of residue with or without added catalyst.

Sanford and Chung (1991) proposed that there was a distinction between two pseudocomponents in the residue fraction, which they called CCR-Pitch and non-CCR-Pitch. They proposed that these components react via different mechanisms. CCR-Pitch, in thermal reactions, was postulated to react to form a coke precursor radical which would eventually become part of the coke. This reaction would involve cleavage of a side chain to produce a coke precursor radical and a distillate precursor radical. Non-CCR-Pitch was proposed to only produce distillate precursors by a similar mechanism. The CCR precursors were presumable polynuclear aromatic groups, but the two psuedocomponents were not defined in terms of chemical structure.

Sanford (1994) performed further investigations on residue conversion and extended the above mechanism. He suggested that the initial bond breakage by homolytic scission of the carbon-carbon bond produced two radical intermediates, a phenyl radical and an aliphatic carbon radical. The phenyl radical would react with a hydrogen atom, which was activated by chemisorption onto a metal sulfide surface, abstracted from a hydrogen donor molecule, or abstracted from $H_2$. These radical intermediates would fragment into gases and distillates according to the following representation of the mechanism (Sanford, 1994):

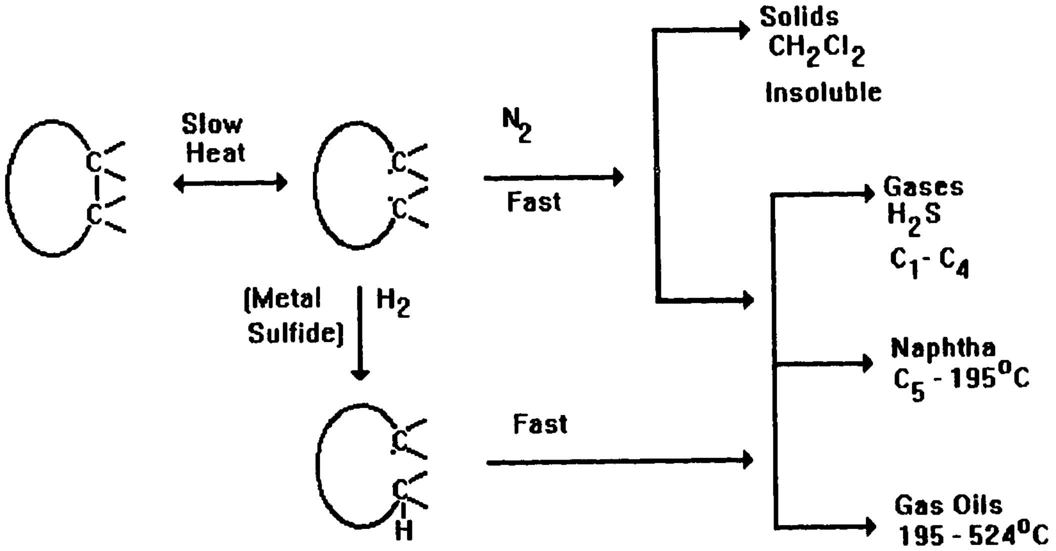


Figure 2.1: Residue Conversion Model Developed by Sanford (1994). Nitrogen simply denotes an inert atmosphere and the inert gas does not participate in the reaction.

These mechanisms derived from Curran's original work were all empirical mechanisms developed to help explain the observations from the experiments on complex feeds. They can all be considered radical capping mechanisms, initiated by the homolytic breaking of covalent bonds to form free radicals. These radicals combine with abstracted hydrogen to produce "capped" molecules (Poutsma, 1990). A general mechanism for radical capping by hydrogen is as follows:

$$R - R \longrightarrow R^{\bullet} + R^{\bullet} \qquad (16)$$

$$R^{\bullet} + H_2 \longrightarrow RH + H^{\bullet} \qquad (17)$$

$$R^{\bullet} + H^{\bullet} \longrightarrow RH \qquad (18)$$

Given reactions (16) through (18), cracking in the presence of hydrogen should be extremely slow since the homolytic cleavage of a carbon-carbon bond is highly energy intensive. Any subsequent chain reaction would then be inhibited by hydrogen (reaction (17)). Experimentally, however, it has been observed that a variety of hydrocarbon compounds show significant reactivity between 400 - 420°C. Alkanes crack at an appreciable rate, for example n-hexadecane had a half life of 3.5 h when hydrocracked in benzene at 430°C (Khorasheh and Gray, 1994). The half life of pure n-hexadecane was much shorter. The difference was due to the solvent and not due to the presence of hydrogen. Table 2.3 lists some representative data concerning the half life of various compounds.

Table 2.3: Half Life of Hydrocarbons in Thermal Cracking

| | First order rate Constant, k, $h^{-1}$ at 430°C | $t_{half}$, h |
|---|---|---|
| Homolytic C-C Breakage (1) | $2.14 \times 10^{-5}$ | $3.4 \times 10^{4}$ |
| Hydrocracking of n-$C_{16}$ in (2) Benzene | 0.2 | 3.5 |
| Thermal Cracking of n-$C_{16}$(3) | 0.35 | 1.9 |
| Hydrocracking of Bitumen(4) | 2.2 | 0.3 |

1. based on initiation rate of n-hexadecane determined by Khorasheh and Gray, 1993a

2. Khorasheh and Gray, 1994

3. Khorasheh and Gray, 1993a

4. Gray, 1994

Table 2.3 gives half lives of n-hexadecane under different conditions. Assuming that the carbon-carbon bonds in complex mixtures are the same as in the model compound, it follows that the rate of initiation in model compounds provides a limit on the rate of homolysis in complex mixtures. In the radical capping mechanism, the rate limiting step is the homolysis of the carbon-carbon bond (reaction (16)) and is equal to the overall rate of cracking of the parent compound. Therefore, it is possible to predict the rate of conversion of carbon-carbon bonds by the radical capping mechanism (or at least indicate the order of magnitude), since it is possible to predict the rate of carbon-carbon bond breakage. From the initiation rate in Table 2.3, the radical capping mechanism gives predictions that are almost three orders of magnitude different from experiments. It must be concluded that the conversion of a feed by a series of homolytic bond cleavages, followed by radical reactions with hydrogen to give stable species would not account for the observed rates.

The typical bond energy that must be overcome for homolytic carbon-carbon bond cleavage is about 345.6 kJ/mole at 25°C (Reusch, 1977). The experimental observations of the activation energy for the initiation reaction ranges from 213 - 398 kJ/mol (Billaud et al., 1988; Khorasheh and Gray, 1993; Sundaram and Froment, 1978). Once formed, radicals react via pathways with much lower energy requirements. Activation energies for β-scission reactions range from 125 - 146 kJ/mol and hydrogen abstraction reactions range from 46 - 71 kJ/mol (Billaud et al., 1988; Khorasheh and Gray, 1993). The high energy requirement for homolytic carbon-carbon bond cleavage is much larger than for subsequent reactions by radicals and, therefore, it would seem impossible that a reaction of commercial interest could proceed by homolytic cleavages only.

Complex feeds such as coals and petroleum residues contain weaker bonds such as carbon-oxygen and carbon-sulfur, and scission of these bonds is sometimes suggested as being responsible for the conversion. Such arguments do not address the failure of the mechanism in model compounds, or its unfavorable energetics even when weak bonds are broken.

The main problem of radical capping is that it does not incorporate the most elementary features of free radical chemistry. It ignores the basic structure and energetics of free radical reactions. Since radical species are highly energetic, short lived and present at very low concentrations, chain reactions are required for radicals to give observable conversions under the conditions used for upgrading of petroleum residues.

Radical reactions consist of three elementary steps: initiation which is often energy intensive, propagation where products are formed without destroying radical species and termination where radicals are consumed. The overall rate of reaction depends on the rate constants of all three steps. The radical capping mechanism does not have proper propagation steps as normally defined, since the hydrogen radicals can only give termination products. In a chain reaction, the initiation step is not necessarily rate limiting, because once formed, a radical can participate in thousands of reactions, each with a much lower energy requirement than homolytic bond cleavage. A chain reaction would occur whether it is initiated by the breakage of a carbon-carbon bond, or by a weak bond such as a peroxide in low temperature polymerization of styrene.

If hydrogen capped radicals to form stable molecules, it would in fact suppress the cracking reactions by shutting down the chain reaction. The work of McMillen et al.

(1987, 1989) suggests that the transfer of hydrogen radicals may be important in taking radicals from large molecules and transferring them to active species. Rather than capping the radicals, this process removes the radicals from some molecules and transfers them to another.

From the above mentioned problems, the simplistic reaction scheme for radical capping is not consistent with the chemistry and energetics of observable free-radical reactions. Chain reactions are the essence of radical reactions which occur at a useful rate, and reactions with hydrogen or tetralin should be interpreted with the context of a chain reaction.

## 2.4 Validation of Liquid Phase Free Radical Mechanism

Besides the empirical studies mentioned in the previous section, there have been many model compound investigations performed at low pressure. Most of these studies were in the gas-phase and were easily interpreted by the Rice-Herzfeld free radical chain mechanism. Recent studies have focused on liquid phase reactions, with the objective of understanding the free radical mechanism at a higher density of reactants. Allen and Gavalas (1984) studied reactions relevant to coal liquefaction. They were interested in the methylene and ether bridged compounds which are common in coal molecules. They mixed various model compounds containing these types of bridges with dialin (1,2-dihydronaphthalene). Under thermal reaction conditions, dialin decomposes via a free radical mechanism giving naphthalene, tetralin and an atomic hydrogen intermediate.

The authors modeled the liquid phase reactions using a free radical mechanism by basing it on the fact that the principle mode of methylene and ether-bridge dissociation under moderate conditions was by atomic displacement reactions with atomic hydrogen. Bond homolysis was negligible due to the activation energy required. Allen and Gavalas found good agreement between the free radical model and the experimental results observed. They concluded that a free radical mechanism can be applied qualitatively to liquid phase reactions in a temperature range of 350 - 400°C.

Similarly, Kanabus-Kaminska et al. (1989) examined solvent effects on the thermochemistry of free radical chain reactions. They found that solvation effects are minimal for the case of non-polar reactants such as hydrocarbons. Regardless of the reactants, the enthalpies of free radical chain reactions will be the same in non-polar solvents as in the gas phase.

From the work of these researchers, it can be concluded that liquid phase pyrolysis or decomposition reactions can follow a free radical chain reaction and that the kinetics of some liquid phase reactions can be related quantitatively to gas phase reactions.

## 2.5 Model Compound Studies with n-Alkanes

Model studies are performed to examine how a representative compound acts under conditions relevant to processing of complex feeds. These findings are then extended to real systems to help identify how the complex mixture reacts. Fabuss et al. (1962, 1964) extended the earlier work of Rice and coworkers to describe high pressure thermal cracking of n-alkanes. They examined n-hexadecane at pressures of 1 - 7 MPa and pyrolysis temperature of 550 - 600°C and proposed a Rice-Herzfeld free radical chain mechanism to explain the observed product distributions. The original mechanism did not explain the observed product distribution completely, so the classical free radical chain mechanism was revised by proposing that parent radicals react via a single-step decomposition to produce a lower alkyl radical:

Hydrogen Abstraction:

$$\text{n-C}_{16} + \text{R}^{\bullet} \longrightarrow \text{R}_1\text{H} + \text{n-C}_{16}^{\bullet} \qquad (19)$$

β-Scission:

$$\text{n-C}_{16}^{\bullet} \longrightarrow \text{1-C}_j\text{H}_{2j} + \text{n-C}_i\text{H}_{2i-1}^{\bullet} \quad (i+j=16) \qquad (20)$$

Hydrogen Abstraction:

$$\text{n-C}_i\text{H}_{2i-1}^{\bullet} + \text{n-C}_{16} \longrightarrow \text{n-C}_i\text{H}_{2i-2} + \text{n-C}_{16}^{\bullet} \qquad (21)$$

Where $R^{\bullet}$ is an n-alkyl radical and $R_1H$ is the corresponding n-alkane. The Fabuss-Smith-Satterfield (F-S-S) mechanism was consistent with the observed equimolar distribution of n-alkanes and α-olefins. Without reaction (21), olefinic products would dominate.

The study of Fabuss et al. (1962, 1964) was followed by other high pressure investigations by Poutsma and Dyer (1982), Kissin (1987), Ford (1986), and Khorasheh and Gray (1993a). Poutsma and Dyer examined the liquid phase thermolysis of 1,3-diphenylpropane and 1,4-diphenylbutane and found that the conversion in the liquid phase was greater than the conversion in the gas phase. The behavior of the model compounds indicated that as conversion increased, secondary consumption of olefinic products was increased. Kissin (1987) investigated the free radical cracking of isoalkanes and described the results by a mechanism similar to Fabuss et al. (1964). Both Kissin (1987) and Ford (1986) found that the isomerization by hydrogen abstraction was much slower than bimolecular hydrogen abstraction. Ford also observed that for the thermal decomposition of n-hexadecane, longer residence times produced a similar product distribution to shorter residence times but there was also evidence of $C_{18}$ - $C_{30}$ compounds. He suggested that at higher conversions the hexadecane radicals not only abstract hydrogen but also react with straight chain alkanes to produce the higher molecular weight compounds.

Khorasheh and Gray (1993a) confirmed the formation of higher molecular weight species during a study of the high pressure thermal cracking of n-hexadecane. They suggested that the species in the $C_{18}$ - $C_{30}$ range were formed by reaction of an olefin with an alkyl radical. Both Ford (1986) and Khorasheh and Gray (1993a) described their model by a modified F-S-S mechanism. The modifications were a result of the following observations: 1. the formation of high-molecular weight alkylhexadecane, 2. formation of lower molecular weight branched alkanes and 3. decreasing molar selectivities for α-olefins with increasing conversions. The model developed by Khorasheh and Gray is as follows:

$$\text{n-C}_{16} \longrightarrow R_1^\bullet + R_2^\bullet \tag{22}$$

$$R^\bullet + \text{n-C}_{16} \longrightarrow \text{R-H} + \text{n-C}_{16}^\bullet \tag{23}$$

$$\text{n-C}_{16}^\bullet \rightleftharpoons \text{n-C}_{16}^\bullet \text{ (isomer)} \tag{24}$$

$$\text{n-C}_{16}^\bullet \longrightarrow \alpha\text{-olefin} + \text{primary n-alkyl radical} \tag{25}$$

$$\text{primary n-alkyl radical} \rightleftharpoons \text{secondary n-alkyl radical (isomer)} \tag{26}$$

$$\text{secondary n-alkyl radical} \rightleftharpoons \text{secondary n-alkyl radical (isomer)} \tag{27}$$

$$\text{n-C}_{16}^\bullet + \alpha\text{-olefin} \longrightarrow \text{higher alkyl radical} \tag{28}$$

$$\text{primary n-alkyl radical} + \alpha\text{-olefin} \longrightarrow \text{higher n-alkyl radical} \tag{29}$$

$$\text{secondary n-alkyl radical} + \alpha\text{-olefin} \longrightarrow \text{higher branched alkyl radical} \tag{30}$$

$$R^\bullet \longrightarrow \alpha\text{-olefin} + \text{primary n-alkyl radical} \tag{31}$$

$$R_i^\bullet + R_j^\bullet \longrightarrow \text{products} \qquad (32)$$

This modified F-S-S free radical chain mechanism takes into account the radical addition reactions that are important at high pressure and moderate temperatures, giving consumption of olefins, but it is only valid at low conversions.

## 2.6 Model Compound Studies with Aromatics

The above studies as well as others (Blouri et al., 1985; Zhou et al., 1986, 1987) confirmed that a free radical chain mechanism can be used to describe the results of liquid phase decomposition of n-alkane model compounds. Poutsma (1990) reviewed model compound studies of reactions of aromatic compounds relevant to coal processing. The literature collected by Poutsma suggests that a free radical chain reaction mechanism can be applied to cracking of liquid hydrocarbons as long as aliphatic carbon was available for reaction. Out of approximately twenty-one mechanisms presented, ten involved aromatics with alkyl side chains or bridges. Of all the compounds containing aliphatic carbon, only toluene did not undergo free radical chain decomposition. The literature collected by Poutsma (1990) suggests that when alkyl groups longer than one carbon are present, thermal decomposition follows a chain reaction. Only the decomposition of aromatic compounds without aliphatic substitutions seems to follow non-chain reaction mechanisms. Without any aliphatic carbon, initial homolytic scission would be difficult and the reaction would tend to be slow or non-existent. Walter and Klein (1995) have also indicated that with a least two consecutive alkyl carbons, β-scission will occur, implying that a free radical chain reaction will result once the radicals have been initiated.

Liquid phase reaction studies on alkylaromatic compounds have been performed primarily at low pressure. For example Savage and Korotney (1990) investigated the pyrolysis of long chain n-alkylbenzenes and developed a descriptive free radical model that was verified by experimental results. Smith and Savage (1991) examined the pyrolysis of polycyclic alkylaromatics to model the reaction pathways of asphaltenes under the same conditions. Smith and Savage (1991) found the same product distribution as Savage and Korotney at short reaction times, but at longer times identified additional products such as pyrene and vinyl pyrene.

Savage and Klein (1985) performed model compound studies on pentadecyl benzene (PDB) in a batch reactor under pyrolysis conditions. From their observations, they developed two possible mechanisms. The first was a retro-ene mechanism and the second was a typical Rice-Herzfeld free radical chain mechanism. Both appeared to follow the first order kinetics observed but the retro-ene mechanism failed to account for all the observed products. The authors deduced that the free radical chain reaction was the best mechanism. They further suggested that the results had relevance to asphaltene reactivity because asphaltenes have aromatic structures with alkyl substituents.

Savage and Klein were not the only authors to relate model compound studies to complex mixtures. Poutsma and Dyer (1982) investigated the liquid phase thermolysis of 1,3-diphenyl propane and 1,4-diphenyl butane and related the observations to coal liquefaction. The main assumption used was that coal has the same type of characteristics observed in the model compound study. The authors suggested an empirical free radical chain mechanism for coal liquefaction based on the results of the model compound investigation (below).

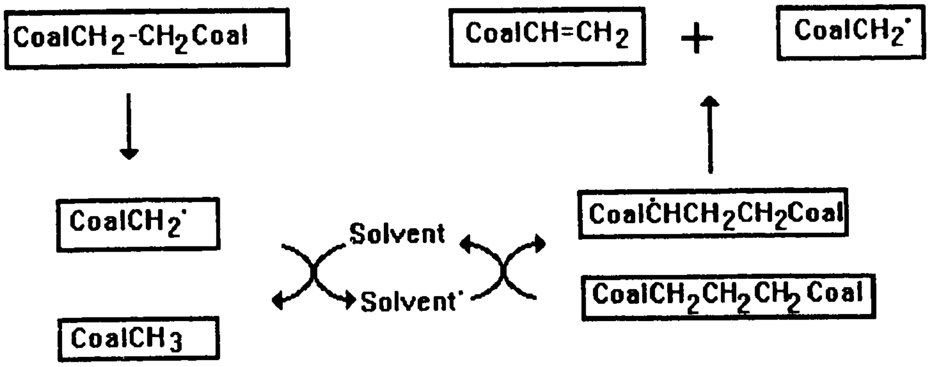


Figure 2.2: Mechanistic Model for Coal Conversion Developed by Poutsma and Dyer (1982)

The solvent derived radicals were assumed to by very mobile and played an active role in shuttling hydrogen to the large coal molecules. The coal species were assumed to be restrained due to the size of the coal matrix. This model was not tested against experiments, but it was significant in identifying β-scission as a propagation step.

Walter and Klein (1995) developed a mechanistic model for the pyrolysis of 4-(1-naphthyl methyl) bibenzyl (NBBM). NBBM's structure contains three aromatic groups linked by alkyl bridges, analogous to structures which are likely to occur in coals or bitumen residues. Walter and Klein indicated that model compound experiments can be used to obtain data for computational modeling of families of reactions in complex mixtures. The model developed consisted of eight reaction families (bond fission, hydrogen abstraction, β-scission, radical ipso substitution, radical elimination, radical hydrogen transfer, radical disproportionation and radical recombination), giving the overall free radical chain mechanism. Upon comparing the computational results from the model and the results for NBBM experiments, Walter and Klein found good agreement, validating their model. Their model provided two major contributions: 1. fundamental kinetic parameters that have a broad application and significance, and 2. insight into pathways and mechanisms during coal liquefaction and residue upgrading.

The models of Savage and Klein (1985), Poutsma and Dyer (1982), and Walter and Klein (1995) implied that a free radical chain mechanism may be valid for heavy oil upgrading and coal liquefaction. An experimental method to test this hypothesis is still lacking.

## 2.7 Reaction Mechanism in Complex Hydrocarbon Mixtures

Despite the volume of information on gas and liquid phase thermal reactions of pure compounds, these results have not been directly applied to complex mixtures of heavy hydrocarbons. Hillewaert et al. (1988) constructed rigorous free radical chain reaction models for naphtha pyrolysis, but this approach is difficult to extend to heavier feeds. Le Page et al. (1987) have hypothesized that asphaltene and resin conversion is by a free radical chain reaction. Similarly, Bunger (1985), Savage and Klein (1985) and Beaton and Bertolacini (1991) have reported that residue conversion is primarily thermal and involves free radical intermediates, however, a chain reaction mechanism is still lacking.

Although a comprehensive mechanism cannot yet be written for the complex mixtures in petroleum residues, simplifications based on the radical capping model (Curran et al., 1967) are commonly invoked as a qualitative framework for interpreting experimental data, for example, by Sanford (1994) and Poutsma (1992).

Wiser et al. (1967) examined the pyrolysis of a high-volatile Utah bituminous coal They observed that as coal was heated slowly at a constant rate, there was a period where volatiles were rapidly evolved at around 400°C, possibly due to decomposition reactions They also observed that the thermal rupture of bonds increased between 350°C and 500°C. In addition, the large amounts of methane, and some ethane and propane evolved suggested that the aromatic clusters within coal may have some short-chain aliphatic linkages. The mechanism deduced from the observations was essentially a Rice-Herzfeld reaction. The initial decomposition involved the thermal rupture of carbon-carbon bonds which linked adjacent aromatic clusters, producing two free radicals. This is followed by a β-scission reaction to produce an olefin and a radical. The reaction is terminated by two radicals adding together to form a product.

McMillen et al. (1987, 1989) performed experiments on coal liquefaction to disprove the radical capping mechanism, using solvent/coal/dinaphthylmethane mixtures as well as a large number of model compounds. McMillen et al. (1989) suggested that hydrogen shuttling may not be merely a scavenging process, but may also induce bond scission. From their experimental observations, they developed a radical hydrogen transfer (RHT) mechanism to describe coal liquefaction. The mechanism involves the transfer of hydrogen in a direct bimolecular process from a cyclohexadienyl carrier radical formed from polynuclear aromatic hydrocarbons (PAH) or coal structures. Although it was not shown in the mechanism, the propagation step RHT cannot occur unless there is initiation such as bond scission by thermolysis or radical disproportionation (McMillen et al., 1987b) The RHT mechanism for coal liquefaction in hydroaromatic solvents is illustrated in Figure 2.3 (McMillen et al., 1987b).

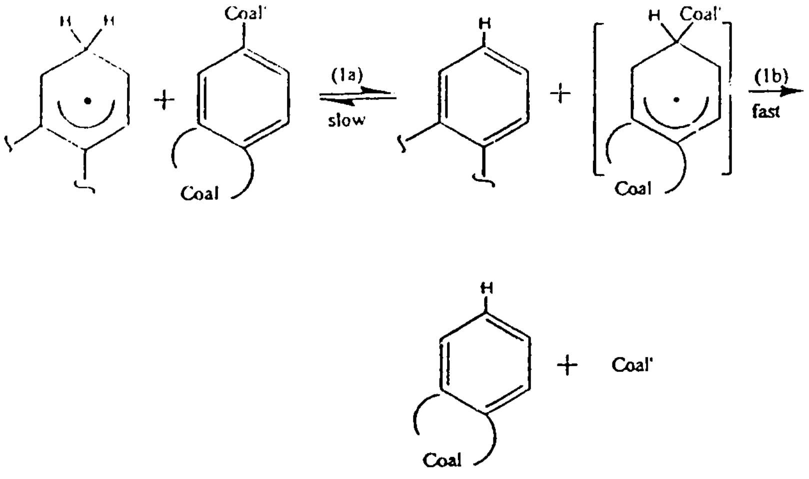


Figure 2.3: The RHT Mechanism for Coal Liquefaction Developed by McMillen et al. (1987b)

Further evidence to support the RHT mechanism was reported by McMillen et al. (1987a). They determined the five most probable mechanisms for non-ionic hydrogen transfer and tried to fit experimental results from model compound decomposition to the mechanisms. They observed that the relative rates of hydrogen transfer, the absence of radical displacement products and the positional preference of hydrogen transfer to 1,2-dinaphthylmethane all lead to the same conclusion: RHT was a substantial and dominant contributor to hydrogen transfer that resulted in the hydrogenolysis of the strongly bound carbon-carbon bonds in coal (McMillen et al., 1987a).

Although some evidence supported the RHT mechanism, it remains controversial. RHT was not dominant under all conditions investigated. There appeared to be a competition between RHT and other hydrogen transfer reactions which shifted as conditions changed (McMillen et al., 1987a). A two step free radical process for hydrogen addition and elimination could give the same products as the RHT (McMillen et al., 1987b). These observations made it difficult to prove which mechanism was the true mechanism for hydrogen transfer within coal liquefaction mixtures. Another problem with the RHT mechanism was that the rate constants reported for model compound cleavage produces half lives of 30 h or greater at 400°C (McMillen et al., 1987a). However, the authors suggested that the reaction would be faster in the presence of coal due to its composition and its tendency to initiate free radical reactions. In addition to the above problems, Autrey et al. (1995) indicated that there was no a priori means of estimating the intrinsic activation barrier for RHT as shown in Figure 2.1. The RHT pathway was difficult to prove since there was much uncertainty in the heats of formation of radical intermediates and there was a lack of absolute rate data. These problems lead Autrey et al. to conclude that the RHT mechanism could not be the dominant hydrogen transfer mechanism and that more conventional radical pathways seem to be responsible for the scission of strong carbon-carbon bonds in coal liquefaction.

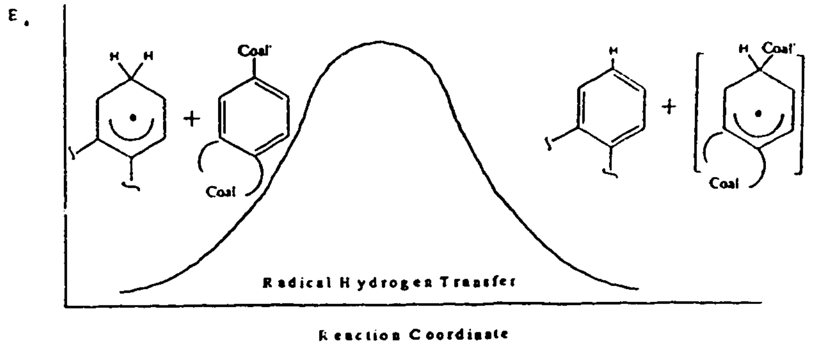


Figure 2.4: Activation Barrier for Radical Hydrogen Transfer (following Autrey et al., 1995)

Because of problems with the RHT model, Malhotra and McMillen (1993) developed a new mechanism for coal liquefaction. Prompted by the lack of correlation between liquefaction effectiveness and the radical scavenging ability of different solvents, and the observed cleavage of relatively strong bonds under liquefaction conditions, they suggested that the solvent or solvent derived radicals would mediate the cleavage of bonds. This model incorporated the RHT mechanism and hence would have similar problems.

In general, model compound studies in the liquid phase at high pressure give results that are consistent with free radical chain reactions so long as aliphatic carbons are present. The main differences between gas phase and liquid phase reactions were solvent interactions and increased importance of bimolecular reactions. These studies have been extended to include complex hydrocarbon mixtures and new radical mechanisms have been developed to explain cleavage of strong carbon-carbon bonds. McMillen et al. (1987, 1989) and Wiser et al. (1967) have proposed chain reaction mechanisms to describe complex mixtures. The energetics of the RHT propagation steps remain controversial, but at least the mechanism contains the key elements of initiation, propagation, and termination.

## 2.8 Solvent Inhibition of Free Radical Reactions

Cracking of residues often occurs in the presence of distillate hydrocarbons, either from the feed mixture or formed as lighter products from cracking of residue molecules. These distillates could have several possible roles, including functioning as a diluent that reduces bimolecular reactions between residue components, acting as a donor of hydrogen if hydroaromatic components are present, or being an active participant in chain reactions. Addition of donor solvents is the basis of one approach to residue upgrading, where blending of residue with compounds such as tetrahydronaphthalene (tetralin) can suppress coke formation. Addition of tetralin can also reduce residue conversion (Thomas et al., 1989).

The earliest work on interactions of free radical chain reactions with diluents was in gas-phase pyrolysis of alkylbenzenes, starting with toluene. Szwarc (1948) proposed a simple model for the pyrolytic decomposition of toluene. His mechanism assumed that the homogeneous gas-phase decomposition was first order since a plot of log k vs. 1/T produced a straight line. The scheme he proposed was:

Initiation:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2^{\bullet} + H^{\bullet} \tag{33}$$

Propagation:

$$H^{\bullet} + C_6H_5CH_3 \longrightarrow H_2 + C_6H_5CH_2^{\bullet} \tag{34}$$

$$H^{\bullet} + C_6H_5CH_3 \longrightarrow C_6H_6 + CH_3^{\bullet} \tag{35}$$

$$CH_3^{\bullet} + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2^{\bullet} \tag{36}$$

Termination:

$$2\,C_6H_5CH_2^{\bullet} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \tag{37}$$

Szwarc indicated that the benzyl radical was very stable due to resonance stabilization. This mechanism was investigated by other researchers (Blades et al., 1954; Takahasi, 1960; Hurd and Macon, 1962; Price, 1962; Brooks et al., 1971) and they discovered some problems. Blades et al. found higher molecular weight products than bibenzyl which implied that $H^{\bullet}$, $CH_3^{\bullet}$ and $C_6H_5CH_2^{\bullet}$ could extract hydrogen at random from not only side chains but from the benzene rings. These observations were later confirmed by Brooks et al. (1971). The first order reaction assumption was clarified by Blades et al. (1954) through their explanation that it depended on the surface of the reactor, contact time and pressure of the system. Slight curvature in the plots of log k vs. 1/T was found by both Blades et al. (1954) and Takahasi (1960), implying that the reaction was not first order. Modifications to the original mechanism were made, but the mechanism described by Szwarc was taken as a general mechanism for toluene decomposition that fitted well with experimental data.

From his initial studies, Szwarc (1949) devised a toluene carrier gas technique to determine the carbon-carbon bond energy of the aliphatic carbon-carbon bond of ethylbenzene. Toluene, used in excess, inhibited free radical chain reactions and suppressed the decomposition of ethylbenzene. The main chain propagating step for decomposition of ethylbenzene involves abstraction of a hydrogen by a methyl radical:

$$CH_3^{\bullet} + C_6H_5CH_2CH_3 \longrightarrow CH_4 + C_6H_5CH_2CH_2^{\bullet} \qquad (38)$$

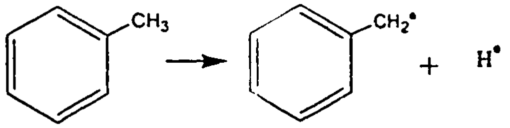
However, in the presence of excess toluene, the methyl radical reacts with toluene as shown below.

$$CH_3^{\bullet} + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2^{\bullet} \qquad (39)$$

In general, $C_6H_5CH_2R \longrightarrow R^{\bullet} + C_6H_5CH_2^{\bullet}$ is followed by the fast reaction of the radical by $R^{\bullet} + C_6H_5CH_3 \longrightarrow RH + C_6H_5CH_2^{\bullet}$ which removes radicals as quickly as they are formed (Leigh and Szwarc, 1952). The overall activation energy for the reaction of dilute ethylbenzene, therefore, gave the carbon-carbon bond energy.

This toluene carrier gas technique could be used to determine if a particular reaction was a free radical chain reaction. Addition of a large excess of toluene to a compound or mixture prior to pyrolysis would suppress the overall conversion. Khorasheh and Gray (1993b) applied this technique to the decomposition of n-hexadecane at 13.8 MPa. They first examined the thermal cracking of toluene and found a number of two-ring compounds in the product mixture, with the dominant compound being 1,2-diphenylethane. These two-ring compounds were formed by termination reactions and radical displacement reactions. The thermal cracking of n-hexadecane in toluene produced a significant increase in the amount of 1,2-diphenylethane which suggested that the concentration of benzyl radicals was increased by the increase in initiation reactions. They found inhibition of the rate of cracking of n-hexadecane with a large excess of toluene, which is consistent with abstraction of benzylic hydrogen from toluene. They developed a simplified mechanism for the reaction of n-hexadecane in toluene, which was used in turn to develop a kinetic model. The model results were similar to the experimental results except for a slight deviation in the distribution of α-olefin products. The detailed mechanism was as follows:

Initiation:



(40)

$$n\text{-}C_{16} \longrightarrow R_i^{\bullet} + R_j^{\bullet} \qquad (41)$$

Rearrangement:

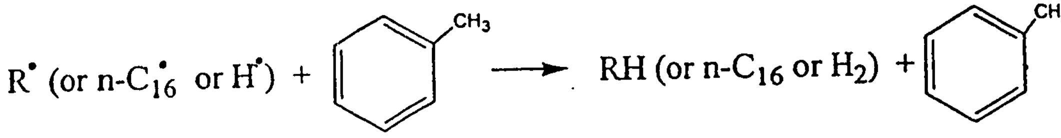
$$\text{Primary } R^{\bullet} \text{ (or } n\text{-}C_{16}^{\bullet}\text{)} \rightleftharpoons \text{Secondary } R^{\bullet} \text{ (or } n\text{-}C_{16}^{\bullet}\text{)} \qquad (42)$$

Propagation:

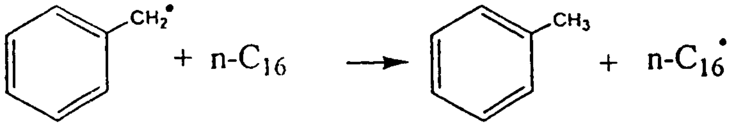
$$R^{\bullet}\text{(or } n\text{-}C_{16}^{\bullet} \text{ or } H^{\bullet}\text{)} + n\text{-}C_{16} \longrightarrow R\text{-}H \text{ (or } n\text{-}C_{16} \text{ or } H_2\text{)} + n\text{-}C_{16}^{\bullet} \qquad (43)$$

$$n\text{-}C_{16}^{\bullet} \longrightarrow R^{\bullet} + \alpha\text{-olefin} \qquad (44)$$

$$R^{\bullet} \longrightarrow R_1^{\bullet} + \alpha\text{-olefin} \qquad (45)$$



(46)



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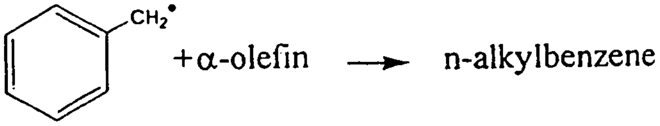
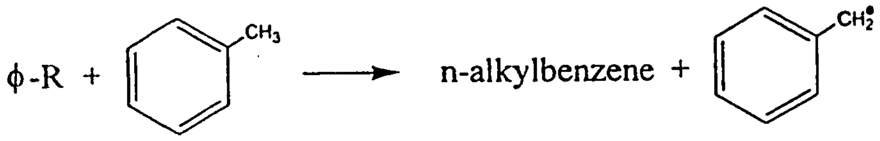


(48)

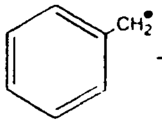
$$\phi\text{-}R^{\bullet} + n\text{-}C_{16} \longrightarrow \text{n-alkylbenzene} + n\text{-}C_{16}^{\bullet} \qquad (49)$$

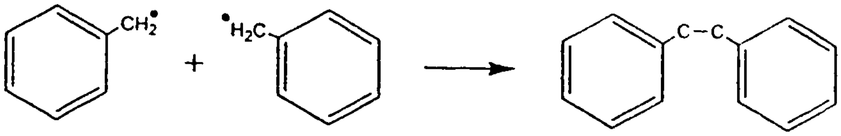


(50)

Termination:

$R^{\bullet}$ (or n-$C_{16}^{\bullet}$ or $\phi$-$R^{\bullet}$ or $H^{\bullet}$) + $R^{\bullet}$(or n-$C_{16}^{\bullet}$ or $\phi$-$R^{\bullet}$ or $H^{\bullet}$) $\longrightarrow$ Products (51)

$R^{\bullet}$ (or n-$C_{16}^{\bullet}$ or $\phi$-$R^{\bullet}$ or $H^{\bullet}$) +  $\longrightarrow$ Products (52)



(53)

Although the toluene carrier gas technique has only been applied to model compounds, it would seem that this technique could be applied to complex mixtures to determine if free radical chain propagation steps are occurring. In the cases where chain propagating steps were relevant, the toluene would inhibit the propagating reactions and decrease the rate of decomposition of the original complex mixture. At high pressure, the concentration of bimolecular termination products would also increase, such as the example of diphenyl ethane observed by Khorasheh and Gray (1993b).

Le Page et al. (1987), Bunger (1985), Savage and Klein (1985) and Beaton and Bertolacini (1991) have hypothesized that residue conversion is by a free radical reaction. However, none of these researchers have indicated what type of free radical mechanism the residue conversion follows. It would seem that the application of the toluene carrier gas technique would help identify if residue converts by a free radical chain reaction.

## 2.9 Olefinic-Addition Reactions in Complex Mixtures

Pyrolysis of n-alkanes and n-alkyl aromatics gives olefins as a major product. Khorasheh and Gray (1993) found that olefins played an important role in the subsequent decomposition of n-hexadecane at high pressure. The pyrolysis of an alkane always gave an olefin even under hydrogen pressure. Khorasheh and Gray (1993c) discovered that the addition of olefins to radicals was more favorable than the hydrogenation of the olefin to an alkane. The olefins tended to couple to radicals and give higher molecular weight compounds. This work suggests that the addition of an olefin compound, such as ethylene (the smallest olefin), to a reaction mixture can be used as a probe for free radical reactions.

Although much research has been performed on the decomposition of paraffins, little work has dealt with olefin mixtures at high pressure. The use of ethylene, a two carbon olefin (or alkene), as a carrier gas requires some knowledge of its decomposition. Boyd et al. (1968) examined the kinetics of ethylene reactions. Ethylene decomposition contains some unique mechanistic problems, two of which are identifying the initiation reaction and the possibility that other types of reactions may occur besides free radical reactions. Boyd et al. determined a list of criteria for ethylene decomposition that a mechanism must satisfy:

1. The main products, ethane and a polymer, and also butane do not show an induction period. Ethane as a major product indicates that ethyl radicals must be one of the chain carrying radicals.

2. The yields of propylene, butene, butadiene, and a second polymer rise linearly with time after an induction period.

3. The rate of all other products increases continuously with time.

4. The rate of main product production was approximately second order with respect to ethylene, except for butadiene which was 1.3 order.

5. Activation energy of the formation of ethane, propylene and butene (about 167.4 J/mole) was much lower than observed for most hydrocarbons.

The mechanism they developed was described as a free radical chain polymerization. Initiation was stated to occur by the interaction of two ethylene molecules (below).

$$C_2H_4 + C_2H_4 \longrightarrow C_2H_3^\bullet + C_2H_5^\bullet \tag{54}$$

$$C_2H_5^\bullet + C_2H_4 \longrightarrow C_2H_6 + C_2H_3^\bullet \tag{55}$$

$$C_2H_5^\bullet + C_2H_4 \longrightarrow C_4H_9^\bullet \tag{56}$$

$$C_2H_3^\bullet + C_2H_4 \longrightarrow C_4H_7^\bullet \tag{57}$$

$$C_4H_7^\bullet + C_2H_4 \longrightarrow C_6H_{11}^\bullet \tag{58}$$

••••••••

$$C_nH_{2n-1}^\bullet + C_2H_4 \longrightarrow C_nH_{2n-2} + C_2H_5^\bullet \tag{59}$$

$$C_4H_9^\bullet + C_2H_4 \longrightarrow C_4H_{10} + C_2H_3^\bullet \tag{60}$$

$$\longrightarrow C_6H_{13}^\bullet \tag{61}$$

••••••••

$$C_nH_{2n-1}^\bullet + C_2H_4 \longrightarrow C_2H_5^\bullet + C_nH_{2n} \tag{62}$$

$$2C_2H_5^\bullet \longrightarrow C_4H_{10} \tag{63}$$

The stable product in reaction (59) would be a diolefin and therefore $n \geq 4$. For example, if $n = 4$, the stable product formed would be a butadiene.

Boyd et al. were the first researchers to examine ethylene pyrolysis in the 500 - 600°C range. Benson and Haugen (1967) examined ethylene pyrolysis in the range of 1227 - 1728°C. They observed a similar product distribution as Boyd et al. (1968) but did not find higher olefins. Kunugi et al. (1969) observed a product distribution consistent with Boyd et al. and produced an extensive mechanism for ethylene pyrolysis in the range of 703 - 854°C. All these studies were performed at higher temperatures than for residue conversion and with pressures at or below atmospheric. However, a pattern seemed to develop out of these studies. As the temperature was decreased, the amount of higher olefins present in the products increased. At residue conversion conditions (400 - 450°C , 8 - 18 MPa), the mechanism developed by Boyd et al. (1968) would contain most of the relevant reactions, but the yield of polymerization species would increase due to the reduced temperature.

## 2.10 Mechanism of Coke Formation

Thermal cracking of residues can lead to coke formation, even in the presence of an active catalyst. The asphaltene fraction is often implicated in coke formation, due to either condensation and cross-linking reactions, or to phase separation (Gray, 1994). The asphaltenes have colloidal properties at moderate temperatures, and if these characteristics persist to reaction temperatures, then colloid-colloid interactions could play a role in coke formations (Storm, 1994, 1995; Takatsuka, 1988).

If coke formation involves free-radical chain reactions, giving higher molecular weight species, then the toluene carrier gas technique should suppress coking. In addition to acting as a radical carrier, a diluent would reduce the concentration of residue species. If coke formation requires bimolecular reactions between residue species, then dilution would reduce the rate of reaction.

## 3.0 Materials and Methods

A Parr high pressure and high temperature bench top reactor (model #4575), operating in a semi batch mode was used for all thermal cracking experiments. The reactor had an approximate internal volume of 500 mL and a maximum pressure rating of 34.5 MPa at 500°C. A diagram of the reactor system can be found in Figure 3.1. The temperature was controlled by a Watlow Microprocessor-based Auto-tuning controller, which was tuned to operate at a constant temperature for the various experiments performed.

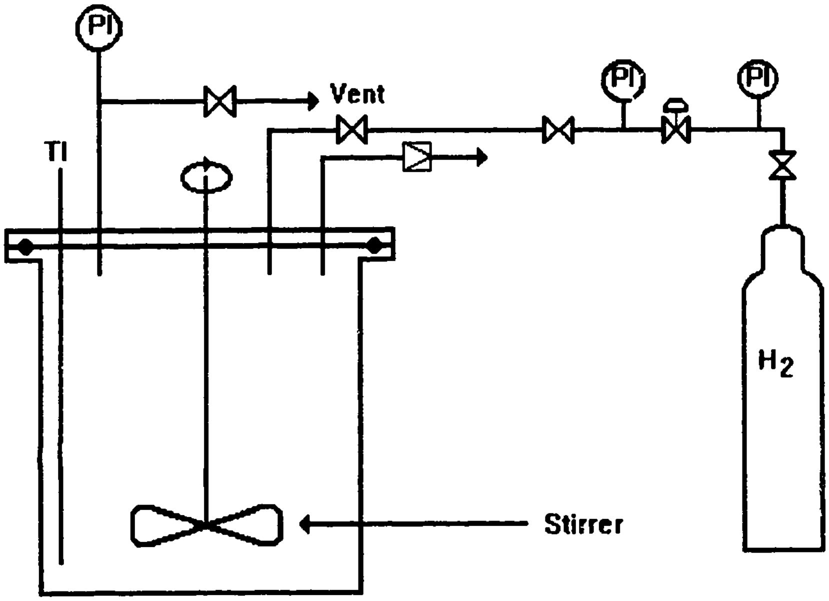


Figure 3.1: Schematic of Reactor System (following Sanford and Chung, 1991)

TI represents the temperature indicator which is a type J thermocouple inserted into the reactor and PI represents the pressure indicators used to monitor the pressure of the reactor and of the hydrogen cylinder.

The 1-methyl naphthalene of 95 % and 98 % purity was obtained from Aldrich and the 1-methyl naphthalene of 99.1 % purity was obtained from TCI America. The 424°C+ topped bitumen was supplied by Syncrude Canada and contained 68.4 % 524°C+ material. The hydrogen gas was obtained from Canadian Liquid Air and the nitrogen and the ethylene gas (polymer grade) were obtained from Matheson.

## 3.1 1-Methyl Naphthalene Diluent Experiments

### 3.1.1 Experimental Design

The purpose of this experiment was to add an alternative radical carrier to the residue. These experiments followed Szwarc (1948) and Khorasheh and Gray (1993) who reacted model compounds in dilute solutions of toluene. The design for this set of experiments was to have 424°C+ bitumen diluted in a solvent that would be in the liquid phase at 400°C and 13.8 MPa.

A simulation package (HYSIM) was used to perform flash calculations using the Peng-Robinson equation of state to determine the appropriate solvent to use, since toluene is not in the liquid phase at the above conditions. The phase behavior of 1-methyl naphthalene was evaluated using HYSIM, because it had similar chemical properties to toluene. Approximately 96 % of the 1-methyl naphthalene was estimated to be in the liquid phase at 400°C and 13.8 MPa. Therefore, this solvent was chosen to be the diluent.

The mole ratio of bitumen to 1-methyl naphthalene in the liquid phase was also estimated using HYSIM. The simulation was based on the volume of the reactor and on the amount of unreacted residue required in the product to do an accurate distillation. It was found through a series of simulations that the best weight ratio was approximately 45 g of bitumen to 225 g of 1-methyl naphthalene (17 wt %). Based on an approximate molecular weight for residue of 1690 g/mole (Gray et al., 1991), the molar concentration of residue (524°C+) in 1-methyl naphthalene solution was 1.2 mole percent. This ratio was chosen to minimize the number of repeat reactions required to produce enough product for analysis and to ensure the safety limits of the batch reactor were maintained. HYSIM was also used to determine the amount of hydrogen to charge into the reactor at room temperature to ensure that at operating temperature (400°C) the reactor was at 13.8 MPa.

Blank and control experiments were required to interpret the results of the 1-methyl naphthalene diluent experiments. The chosen reactions are depicted in Table 3.1 as reactions 1 and 3. Reaction 1 was a blank experiment with pure 1-methyl naphthalene. This was used to interpret the GC results obtained for the termination product from the 1-methyl naphthalene diluent experiments. Reaction 3 was a control experiment with undiluted residue and was compared with the residue conversion for the 1-methyl naphthalene diluent experiments. The conditions for the 1-methyl naphthalene experiments are shown in Table 3.1. Series 1, 2, 3, and 4 used 1-methyl naphthalene with a purity of 98 %. Series 5 used a different batch of 1-methyl naphthalene with a purity of 95 % and series 6 used a third batch of 1-methyl naphthalene with a purity of 99.1 %. The specific reaction conditions for each series can be found in Appendix A.

In each experiment the reactor temperature was held at 400°C for one hour. The timing for the reaction (i.e. time zero) was started as soon as the reactor reached the operating temperature. Although reactions must have started during reactor heating, the time-temperature history of each product sample was identical. The heating period for each residue in 1-methyl naphthalene series was 104.4 ± 1.[illegible] min. There was only a slight variation in the heating periods, therefore, reactions during non-isothermal heating would have no effect on comparisons between the experiments.

Table 3.1: Experiments Performed for the 1-Methyl Naphthalene Diluent Series

| Reaction Number | Amount of Feed Bitumen | Amount of 1-Methyl Naphthalene | Reaction Temperature and Pressure | Reaction Time |
|---|---|---|---|---|
| Rxn 1 | 0.0 g | 225 mL | 400°C and 13.8 MPa | 1 h |
| Rxn 2 | 45 g | 225 mL | 400°C and 13.8 MPa | 1 h |
| Rxn 3 | 125 g | 0.0 mL | 400°C and 13.8 MPa | 1 h |

### 3.1.2 Experimental Procedure

The experimental procedure for the 1-methyl naphthalene diluent experiments was as follows. The desired amount of feed bitumen and 1-methyl naphthalene were placed into the batch reactor at room temperature (see Table 3.1 for specific conditions). The reactor was then sealed using a torque wrench at a maximum torque of 107 N. A pressure test was performed at 13.8 MPa using hydrogen to ensure that there were no leaks in the system. If the reactor sealed properly, the hydrogen gas was discharged to remove any air that was present in the reactor. The hydrogen was vented carefully into the knockout drum since hydrogen is explosive over a wide range of concentrations. The gas was also checked to ensure that no liquid was being removed with the hydrogen. The reactor was charged with hydrogen once more and was then vented to remove any residual air. Enough hydrogen was recharged into the reactor to ensure that at operating temperature, the pressure within the reactor would be close to the desired operating pressure of 13.8 MPa.

Once the gas was added, the reactor was heated to 400°C and the pressure was adjusted to the correct operating pressure by adding or removing hydrogen from the reactor. The reactor took approximately one hour to heat to 400°C at which temperature the timing for the reaction was started. The reaction time was one hour during which reaction parameters of temperature, pressure, stirring speed and time were recorded. After one hour the heaters were shut off and the reactor was cooled. The following day, the reactor was depressurized and opened to remove the liquid products for analysis. The reactor walls were scraped to remove as much of the liquid product as possible. The reactor was then cleaned with methylene chloride and scrubbed to remove any deposits.

## 3.2 Ethylene Addition Experiment

### 3.2.1 Experimental Design

The purpose of this experiment was to add an olefin to probe for the addition of carbon chains to residue material. This approach followed the results obtained by Khorasheh and Gray (1993) who saw that when olefins were formed they tended to attach themselves to other radicals to produce higher carbon number species than the original compound. The smallest olefin available is ethylene, which is a gas at room temperature and was used in these experiments.

A HYSIM simulation was performed to determine the amount of ethylene to charge into the reactor at room temperature to ensure that at 400°C the reactor pressure was at 10.7 MPa. The lower pressure was used since there was a restriction on the available pressure in the ethylene cylinder (maximum pressure was 8.3 MPa). The amount of residue placed in the reactor was 125 g following the results of the HYSIM simulation for 1-methyl naphthalene blank experiments.

The blank and control experiments chosen to compare to the ethylene addition experiments are shown in Table 3.2 as reactions 1 and 3. The blank reaction, reaction 1, consisted of heating pure ethylene in the reactor to determine if any decomposition or polymerization occurred. The control experiment, reaction 3, was performed to show how the residue reacts in an inert atmosphere of nitrogen. Both experiments were compared with the results of the ethylene addition experiment, reaction 2. The conditions for the ethylene addition experiments are depicted in Table 3.2.

Table 3.2: Experiments Performed for the Ethylene Addition Series

| Reaction Number | Amount of Feed Bitumen | Pressure of Gas charged in Reactor at Room Temp. | Reaction Temperature and Pressure | Reaction Time |
|---|---|---|---|---|
| Rxn 1 | 0.0 | 5.2 MPa Ethylene | 400°C and 10.7 MPa | 0.5 h |
| Rxn 2 | 125 g | 5.2 MPa Ethylene | 400°C and 10.7 MPa | 0.5 h |
| Rxn 3 | 125 g | 4.1 MPa Nitrogen | 400°C and 10.7 MPa | 0.5 h |

### 3.2.2 Experimental Procedure

The procedure used for the ethylene addition experiments was similar to the 1-methyl naphthalene diluent experiments. The minor differences were that the gas used was either ethylene or nitrogen and no solvent was added to the system. Also, the reaction time was shortened to 30 min because there was a chance for ethylene to polymerize.

## 3.3 Coking Experiments with Nitrogen

### 3.3.1 Experimental Design

The purpose of the coking experiments was to examine the effect of diluting the residue with a free radical acceptor; 1-methyl naphthalene. These experiments were designed based on the two previous sections. The blank experiment with solvent is shown in Table 3.3 as reaction 1. Reaction 1 was performed to examine the termination products derived from 1-methyl naphthalene under nitrogen pressure and to examine the amount of solids (i.e. coke) formed from the pure solvent. The control experiment, reaction 3, was not repeated for this set of experiments since it had already been performed for the ethylene addition experiments. The products from that experiment were used to quantify the amount of solids formed during reaction. Table 3.3 indicates the conditions used for the coking experiments.

Table 3.3 Experiments Performed for the Coking Experiments Under Nitrogen Pressure

| Reaction Number | Amount of Feed Bitumen | Amount of 1-MN. | Reaction Temperature and Pressure | Reaction Time |
|---|---|---|---|---|
| Rxn 1 | 0.0 | 125 mL | 400°C and 10.7 MPa | 0.5 h |
| Rxn 2 | 45 g | 225 mL | 400°C and 10.7 MPa | 0.5 h |
| Rxn 3 | 125 g | 0.0 | 400°C and 10.7 MPa | 0.5 h |

### 3.3.2 Experimental Procedure

The procedure used for the coking experiments was similar to the 1-methyl naphthalene diluent experiments. The reaction time and the pressure, however, were reduced to 30 min and 10.7 MPa nitrogen pressure, respectively.

## 3.4 Analysis

The liquid products from the 1-methyl naphthalene diluent experiments and the ethylene addition experiments were sent to Syncrude Research for distillation into the desired cuts. Two distillation procedures were used in series. Spinning band distillation was done at atmospheric pressure to provide two cuts, IBP - 343°C and 343°C+ material. Five different spinning band distillations were required to distill all the product from the residue in 1-methyl naphthalene diluent experiments. The pooled 343°C+ material was then distilled using ASTM D-1160 under vacuum to obtain 343 - 524°C and 524°C+ cuts. Since only two cuts were desired, IBP - 524°C and the 524°C+, the other cuts were mixed back together. The 524°C+ cut was filtered through a 0.22 μm Millipore filter, using methylene chloride as a solvent, to remove any coke within the fraction. The filtered coke was dried and weighed to determine coke and mineral content. By correcting for coke formation, it is possible to accurately calculate residue conversion to lighter fractions. Similarly, the undistilled products from the coking experiments were also filtered using the same method.

The products from the 1-methyl naphthalene diluent experiments and the filtered products from the coking experiments were analyzed by a Hewlett Packard 5890 GC using an HP-1 crosslinked methyl silicone gum column. The column was 30 m in length, had an ID of 0.25 mm and a film thickness of 0.25 μm. The temperature program for the GC was: initial oven temperature was 50°C, the oven was heated up to 300°C at a rate of 5°C/minute, and was held at 300°C for 15 minutes. The detector and injector temperatures were held constant at 310°C. The GC was operated in split mode with the ratio of split to detector being 4.6. Each sample injection required approximately 65 minutes for completion. An internal standard of phenanthrene was used to ensure that the comparisons of the peak areas were accurate (Appendix B shows the results from the injections). The chromatograms from each sample were used to determine the relative change in termination products between the different experiments. Appendix C contains detailed calculations. A sample from the 1-methyl naphthalene diluent experiments and a sample of unreacted 1-methyl naphthalene was sent for GC-MS analysis in the Department of Chemistry, University of Alberta.

The filtered residue fractions from the ethylene addition experiments were sent for carbon-13 NMR analysis to look for carbon chain addition to residue radicals. The carbon-13 NMR was performed using a 200 MHz Bruker WH-200 instrument and a one second pulse delay was used to ensure quantitative integration of the signals. The solvent used was deuterated chloroform, the relaxation reagent was chromium tris-acetyl acetonate and the internal standard was TMS. Over 1000 scans were performed to ensure the accuracy of the integration.

The different areas of the spectra were calculated based on the method of Young and Galya (1984) and Gray (1994). The aromatic and aliphatic fractions of each sample were determined using the relative heights of the integration line. The area under the spectra was calculated using Sigma Scan (Jandel Scientific) and the percentage of carbon within that range was calculated. The paraffinic fraction of the spectra was determined by the area of the sharp peaks in the 22.5 - 37 ppm range plus the two peaks in the 37 - 60 ppm range. Once the paraffinic fraction was obtained, the naphthenic fraction could be found by subtracting the paraffinic fraction from the total aliphatic fraction.

The spectra was divided into 8 different bands according to the following list to calculate the relative amount of carbon in each range (from Gray, 1994):

| Band | Range, ppm | Carbon Structure |
|---|---|---|
| 1 | 11 - 15 | $\gamma$-methyl |
| 2 | 15 - 18 | $\beta$-methyl |
| 3 | 18 - 22.5 | $\alpha$-methyl |
| 4 | 22.5 - 37 | total methylene ($CH_2$) |
| 5 | 37 - 60 | methyne (CH) |
| 6 | 100 - 129.5 | $C_{aromatic}$-H |
| 7 | 129.5 - 140 | $C_{aromatic}$-C |
| 8 | 140 - 160 | $C_{aromatic}$-O,N,S |

# 4.0 Results and Discussion

## 4.1 1-Methyl Naphthalene Diluent Experiments

### 4.1.1 Conversion of Residue

Each sample for distillation was obtained by pooling products from 2 repeat experiments (for undiluted residue) or 5 repeat experiments (residue in 1-methyl naphthalene). The initial residue fraction in the feed bitumen was 68.4 %, so that the concentration of the residue in the liquid feed was 11.7 % after dilution with 1-methyl naphthalene. The conversion of the residue was calculated from the reactor data and distillation data found in Appendix B. Conversions were obtained using the conversion formula as follows:

$$Conversion = \frac{mass\ of\ residue\ in\ initial\ sample - mass\ of\ residue\ in\ product}{mass\ of\ residue\ in\ initial\ sample} \qquad (64)$$

A sample calculation for conversion determination can be found in Appendix C. This formula can be used without correction for coke formation since virtually no coke was formed in experiments with a hydrogen atmosphere (Appendix B). If the reaction was first order, no change in conversion would be found between the undiluted experiments and the diluted experiments. However, if though dilution, there was a change in the conversion, then the reaction cannot be first order.

The conversion of the residue material for undiluted residue experiments under hydrogen pressure was found to be reproducible to within ± 2 % at 48.6 % conversion. The conversion of residue upon dilution with 1-methyl naphthalene (1-MN) was reduced, giving conversions ranging from 1.5 to 41.6 %. The results obtained for both sets of experiments are listed in Table 4.1.

Table 4.1: Conversion of the Residue Fraction with Hydrogen Atmosphere

| Experiment Type and # | # of Reactor Expts Mixed | Conversion of Residue Material, % |
|---|---|---|
| Undiluted Residue Series 1 | 2 | 50.3 % |
| Undiluted Residue Series 3 | 2 | 48.6 % |
| Undiluted Residue Series 5 | 2 | 46.9 % |
| Residue in 1-MN Series 1 | 5 | 1.5 % |
| Residue in 1-MN Series 4 | 5 | 26.8 % |
| Residue in 1-MN Series 5 | 5 | 38.9 % |
| Residue in 1-MN Series 6 | 5 | 41.6 % |

The total liquid product (TLP) for each 1-methyl naphthalene diluted experiment was approximately 98 % of the feed material. The large percentage recovery was mainly due to the low viscosity of the product which made it easier to remove from the reactor. The viscosity of the TLP of the undiluted residue experiments was higher than the diluted experiments, which made removing all the product difficult. The reactor was scraped with a spatula to remove as much product as possible. The TLP recovered for the undiluted experiments was about of 86 % of the original feed. The higher losses were more likely due to gas formation and evaporation of light products, which were more important without diluent. An overall material balance for the experiments was not made since the gas was not analyzed. Quantitative measurements of gas yields are very difficult in such batch reactors since it is difficult to obtain an accurate measure of the volatile's mass. Analyzing the gas would also be problematic since the $C_4$, $C_5$ and $C_6$ fraction of the gas would absorb onto the wall of the sampling bag. Therefore, it was impossible to determine if the decrease in mass was due to gas evolution. Even if gas analysis was possible, the experimental design was to only examine the effect of the solvent on the residue and not to perform detailed kinetic calculation on the decomposition of residues.

Even though four independent series of 5 experiments for the conversion of residue in 1-methyl naphthalene showed suppression of conversion, there was a large variance in the results. This variation could be due to several factors:

1. Multiple reactions: The product from each of five reactions performed for series 6 was analyzed by GC. There was little variance in the amount of 1-methyl naphthalene derived termination products (Appendix B). This result indicated that each reaction probably converted the same amount of residue and hence blending could not account for the differences in residue conversion. By averaging several sets of reaction products together, blending of products should have actually reduced the variability of the residue conversion.

2. Distillation Analysis: Five spinning band distillations of 1-methyl naphthalene diluted residue were required to produce enough sample for one D-1160 distillation. Loss of sample during handling and transfer could result in inaccuracies in weights, particularly mass of residue. Errors due to distillation were small when examining the undiluted residue experiments. However, when looking at the D-1160 results for the diluted experiments there appears to be a discrepancy in the results for series one (Table 4.2).

Table 4.2: Summary of D-1160 Results for the Diluted Experiments

| Series Number | Weight Percent in 343 - 524°C fraction | Weight Percent in the 524°C+ fraction |
|---|---|---|
| Series 1 | 18.03 | 81.12 |
| Series 4 | 43.22 | 54.66 |
| Series 5 | 40.50 | 57.07 |
| Series 6 | 42.97 | 54.92 |

Table 4.2 shows that there was an anomaly in the D-1160 distillation for Series 1. The measured yield of gas oil (343 - 524°C) from Series 1 was substantially lower than the other results. Data from Series 4, 5 and 6 were consistent with previous work in that the 343 - 524°C fraction was not cracked more than the residue (Nagaishi et al., 1995). Based on the results from the D-1160 distillation, the result from Series 1 was treated as an outlier. This observation shows that the D-1160 distillation was likely a significant factor in the variability of residue conversion.

3. Purity of the solvent: The main contaminant in the solvent was found using GC-MS based on the mass spectra. The contaminant appeared at a retention time of 23.7 min and was a branched alkane with a probable structure of 3-ethyl-3-methyl dodecane based on mass spectra and on boiling point. This contaminant was made up of approximately 0.3 % of the 98% pure 1-methyl naphthalene, and it was present in all batches of 1-methyl naphthalene. Minor contaminants were not abundant enough to be identified.

After examining the results produced from the 95 % pure solvent (series 5), it was thought that purity played an important role in determining conversion. An experiment was performed using 99.1 % pure solvent and a conversion of 41.6 % was found. Although there appeared to be no correlation between solvent purity and conversion, minor components (or impurities) within the solvent could sensitize the solvent to free radical reactions. Therefore, the role of solvent impurities cannot be ruled out, but it is difficult to conclude that the minor components will sensitize the bitumen since bitumen is a complex mixture with many components.

Another possibility was that the purity of the solvent might vary between the bottles used for series of experiments. Each bottle used in series 6 was tested and it was found that the concentration of 1-methyl naphthalene in the bottles were extremely close to one another (99.09 ± 0.052 %). It was concluded that using different bottles of solvent probably did not play a role in the variations in conversion.

In addition, the solvent might have been photosensitive and subject to photo-oxidization. However, upon leaving a sample of the solvent under fluorescent lights for almost a month, the lack of colored-complexes indicated that photo-oxidation of the solvent was not sign[illegible] Therefore, it was unlikely that this type of contamination would affect the conversion of the residue material.

4. Oxygen: Traces of oxygen in the reactor would help to initiate the decomposition of the residue; thereby changing the apparent residue conversion. Although the head space of the reactor was purged twice with hydrogen, oxygen would remain in solution in the liquid phase and as small bubbles. The ratio of oxygen trapped in the reactor as small bubbles and dissolved in the liquid to residue would tend to increase with the volume of solvent, and this contamination may alter free radical reactions. Leathard and Purnell (1970) observed that trace amounts of oxygen appeared to accelerate paraffin pyrolysis reactions and the effect of oxygen was more pronounced at higher concentrations of oxygen. Fabuss et al. (1964) indicated that one major source of misleading results in batch reactor studies of free radical chain cracking is the presence of air trapped in the reactor. They found an increase in cracking reactions as a result of the trapped air. They suggested two methods of removing the trapped air: 1. place the

hydrocarbon in the reactor and alternatively freeze and thaw it under vacuum or 2. flush the sealed reactor with an inert gas and close the reactor under inert gas pressure (Fabuss et al., 1964). One other way to reduce the amount of oxygen in the batch reactor would be to use a catalyst. The catalyst would scavenge the oxygen within the reactor.

The procedure used in this experiment was similar to the second method where the reactor was purged twice with hydrogen before performing the experiment. As mentioned above, if there were any traces of oxygen (or air) left in the reactor after purging, an increase in the conversion would be observed due to oxygen initiation of reactions.

To test this hypothesis, solvent was placed inside the reactor and the reactor was not purged before the experiment. This experiment would determine if oxygen affected the amount of termination products found after reaction. If an increase in the termination products was found when oxygen was present within the reactor, then it could be concluded that upon adding residue to the system, the conversion of the residue would also increase. The results found for the pure solvent experiments are listed in Table 4.3.

Table 4.3: Experiments Performed With and Without Purging Using 99.1% Pure Solvent

| Experiment Type | Amount of Termination Product Found (g of termination product / g of 1-MN) |
|---|---|
| Air Purged from the Reactor Before Reaction | 0.565 E-3 |
| Air Not Purged from the Reactor Before Reaction | 4.39 E-3 |

A 7.8 fold increase in termination products was observed when the air was not purged from the reactor. Therefore, this observation implies that when residue is added to the mixture, traces of oxygen present in the reactor would tend to increase the reactivity of the residue and would increase the conversion. As mentioned earlier though, the blending of several sets of reaction products together should have actually reduced the variability of the residue conversion.

5. Heating and Reactor Wall Effects: As mention in Chapter 3, the time-temperature history of each reaction was approximately the same. For the residue in 1-methyl naphthalene experiments the mean heating time was 104.4 ± 1.1 min, which was similar to the pure 1-methyl naphthalene experiments (mean heating time of 99.3 ± 1.2 min with an outlier of 207 min due to a heater problem). Not all the starting times were recorded for the undiluted bitumen case, hence, a total comparison could not be made. Although there is some variability in the heating time, two or more different experiments are being mixed to obtain one product which would tend to balance any difference in the time-temperature history.

The reactor wall could tend to act as a catalyst during reactions. Any change in the wall effect would only be a problem during the first few experiments since the wall had not been sulfided or covered with coke. After the first few experiments, there would be no change in the wall effects, ensuring that any increased activity due to the walls was similar in subsequent reactions.

All of the above factors could contribute to the observed differences in residue conversion, but based on the distillation results, the D-1160 likely accounted for the majority of the variability in the conversion data. In any case, the addition of 1-methyl naphthalene solvent did significantly suppress conversion of residue, relative to control experiments. Even with the variability observed, the diluted experiments consistently gave lower conversions than the control experiments. Treating the 1.5 % conversion value as an outlier due to anomalous distillation results, gave an average conversion for the diluted experiments of 35.8 % which was significantly lower than the average conversion of 48.6 % for the control experiments.

The conversion of the residue for the undiluted experiments was higher at 48.6 % than the value reported by Sanford and Chung (1991). For example, at 400°C and 60 min reaction time under 15.5 MPa hydrogen pressure in a 1L batch reactor, they reported a 37 % conversion of the residue from whole Athabasca bitumen. Sanford and Chung reported a lower value for the conversion of Athabasca bitumen, but this was expected since they were operating at a higher hydrogen pressure and were using a more dilute bitumen. A topped bitumen (similar to the bitumen used in these experiments) has a much higher residue content than a whole bitumen.

The conversion of residue in the 1-methyl naphthalene experiments was expected to be lower than the conversion of the undiluted residue, based on work by Khorasheh and Gray (1993) and Szwarc (1949) who found that the solvent reacted quickly with the initiated radicals. The difference between the conversions of the undiluted residue and residue in 1-methyl naphthalene was smaller than the change observed by Thomas et al. (1989). They found a drop in conversion of residue when they added 1,2,3,4-tetrahydronaphthalene (TN) to Safaniya vacuum residue (SVR). The conversion of the pure SVR at 410°C and 10 MPa with a reaction time of 15 min was 28.7 %. This conversion dropped to about 9 % when a 1:1 ratio of SVR to TN was reacted under the same conditions. The dramatic effect of tetralin at this relatively low concentration could be due to a combination of radical scavenging and donation of hydrogen.

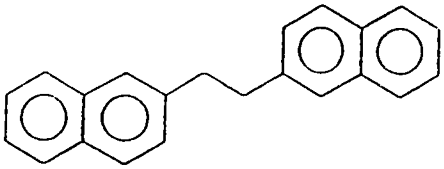
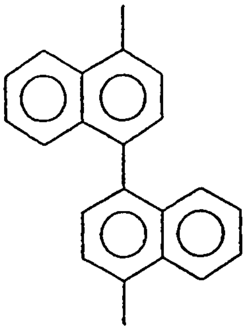
Since suppression of residue conversion was found upon adding a solvent, the first part of the hypothesis was confirmed.

### 4.1.2 1-Methyl Naphthalene Derived Termination Products

The reaction products from pure 1-methyl naphthalene and residue in 1-methyl naphthalene were analyzed by GC as described in Chapter 3. A set of peaks appeared in the GC chromatogram from all of the samples at a retention time of around 46 min as shown in Figure 4.1. These peaks were tentatively identified as the termination products produced by cracking of 1-methyl naphthalene, since they were not present in the unreacted solvent. Adding residue did not change the appearance of the 1-methyl naphthalene termination product peaks, but the area of the peaks did increase. The termination products were analyzed using GC-MS and the most likely structures can be found in Table 4.4. These structures were based on the MS fragmentation. All of the termination products had a molecular weight of 282 Da, corresponding to two units of 1-methyl naphthalene linked together.

Figure 4.1 shows four other peaks due to termination products. These peaks were probably isomers of 4,4'-dimethyl-1,1'-binaphthyl based on the mass spectra. The isomers could result from the resonance forms of the 1-methyl naphthalene radical. They all had a dimethyl dinaphthalene type structure with molar mass of 282 Da. To obtain dimethyl dinaphthalene termination products, radical-radical coupling must be followed by a hydrogen transfer step.

Table 4.4 Termination Products Derived by 1-Methyl Naphthalene as Determined by GC-MS

| | Termination Product Name | Chemical Structure |
|---|---|---|
| I | 2,2'-(1,2-ethanediyl)bis-naphthalene |  |
| II | 4,4'-dimethyl-1,1'-binaphthyl |  |

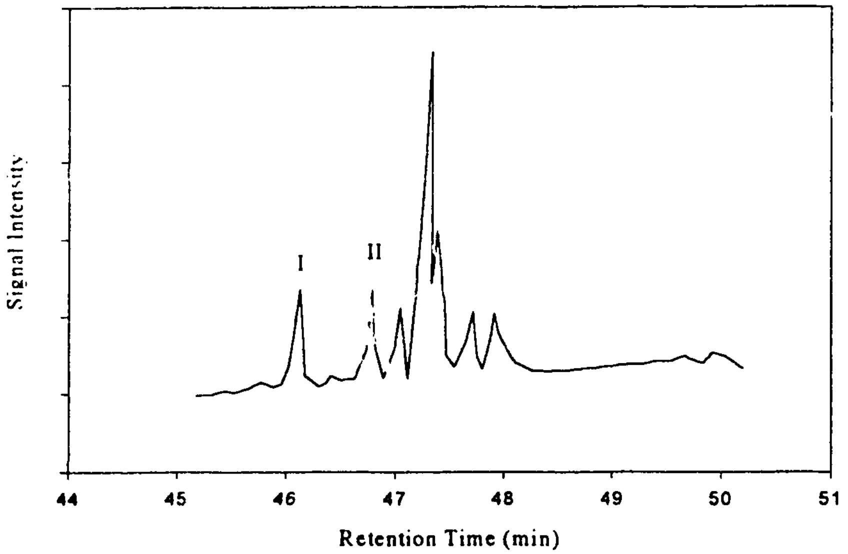
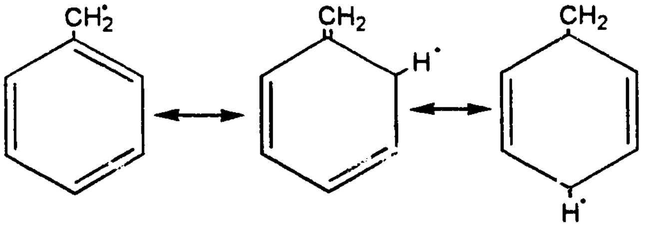
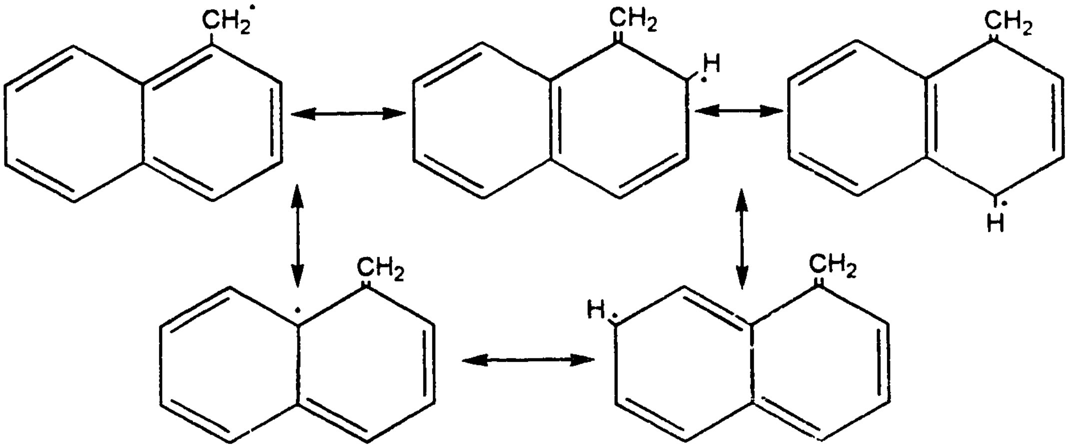


Figure 4.1: Chromatogram of Termination Products

Benzyl radicals are more stable than alkyl radicals because of resonance between the possible structures shown below. The resonance lowers the energy content thereby making the radical more stable (Morrison and Boyd, 1973).



The radical is not tied to the side chain but can delocalize itself and be distributed around the ring. The 1-methyl naphthalene radical would delocalize itself by the same mechanism.



The above resonance structures could give rise to different termination products through radical recombination. Dinaphthyl ethane is only one structure that can be formed. A number of dimethyl binaphthyl products could also be formed.

Addition of the residue increased the concentration of termination products. This increase was quantified by determining the ratio between the termination products produced by residue in 1-methyl naphthalene to the termination products produced by pure 1-methyl naphthalene. This ratio was corrected for the background contribution of the residue, as described in Appendix C. Using the tabulated GC data found in Appendix B, the results for the total termination products are listed in Table 4.5. Sample calculations can be found in Appendix C. Based on the mean concentrations of termination products, the addition of residue increased the concentration of termination products by a factor of 5.9. This increase was consistent with rapid abstraction of hydrogen from the solvent by bitumen radicals, giving an elevated concentrations of 1-methyl naphthalene radicals. Termination products would reform when two radicals recombine, therefore, a 5.9 fold increase in termination products indicated an increase in 1-methyl naphthalene radicals of $(5.9)^{1/2}$ or 2.4 times.

Table 4.5: Ratio of Termination Products From Residue in 1-Methyl Naphthalene Experiments to Pure 1-Methyl Naphthalene Experiments

| Rxn Description and Series | # of Reactor Expts Mixed | Termination Products in Sample g/g (n=2) | Termination Products in Sample Mean | Correction for Residue Contribution | Ratio of Residue in 1-MN to Pure 1-MN |
|---|---|---|---|---|---|
| Pure 1-MN (1) | 1 | 0.320 E-3 | 0.224 E-3 | ——— | 5.88 |
| Pure 1-MN (4) | 1 | 0.128 E-3 | g/g 1-MN | | |
| | | | | | |
| Residue in 1-MN (1) | 5 | 1.23 E-3 | 1.63 E-3 | 1.32 E-3<br>g/g 1-MN | |
| Residue in 1-MN (4) | 5 | 2.03 E-3 | g/g Mixture | | |
| | | | | | |
| Correction for Background signal for Residue | | | | | |
| Undiluted Residue (1) | 2 | 0.461 E-3 | | | |
| Undiluted Residue (3) | 2 | 0.597 E-3 | 0.535 E-3 | | |
| Undiluted Residue (5) | 2 | 0.548 E-3 | g/g Mixture | | |

These data were based on two GC injections for every sample. A third blank experiment using 1-methyl naphthalene was performed, but it gave five times more termination products then the other samples, so it was treated as an outlier. A possible reason for the higher concentration of termination products may be that the experiment was unusually contaminated with oxygen. Series 5 of the diluted experiments gave inconsistent results between repeat injections and was not included in the calculations.

The ratio of concentration of dinaphthyl ethane, with a likely structure of 2,2'-(1,2-ethanediyl)bis-naphthalene, was also calculated (Table 4.6). This compound was the most abundant termination product in the majority of the samples. The chromatogram depicted in Figure 4.1 showed that other termination products were particularly abundant. However, this was not the case in all the samples, hence the dinaphthyl ethane was chosen. It eluted with a retention time of 46.1 min, as depicted on the chromatogram (Figure 4.1) with the roman numeral I. This peak (I) was chosen over the other peaks which were not abundant in all the samples.

Table 4.6: Ratio of Diphenyl Ethane Found in Residue in 1-Methyl Naphthalene Experiments to Pure 1-Methyl Naphthalene Experiments

| Reaction Description | Series Number | # of Reactor Expts Mixed | Termination Products in Sample g/g (n=2) | Termination Products in Sample Mean | Ratio of Residue in 1-MN to Pure 1-MN |
|---|---|---|---|---|---|
| Pure 1-MN | 1 | 1 | 1.33 E-4 | 0.902 E-4 | 3.64 |
| Pure 1-MN | 4 | 1 | 0.473 E-4 | g/g 1-MN | |
| | | | | | |
| Residue in 1-MN | 1 | 5 | 1.93 E-4 | 3.29 E-4 | |
| Residue in 1-MN | 4 | 5 | 3.52 E-4 | g/g 1-MN | |

The difference between the concentration of termination products found in pure 1-methyl naphthalene and the concentration of termination products found in residue reacted in 1-

methyl naphthalene was expected based on the results of Khorasheh and Gray (1993). They found that a large amount of toluene derived termination products were formed due to the decomposition of 1-hexadecane. The termination products from a solvent would increase upon adding a dilute species which would decompose at reaction conditions thereby initiating the formation of free radicals. This increase in termination products was observed in the experiments with added residue, therefore, the second part of the hypothesis was confirmed.

The overall hypothesis that bitumen converts via a free radical chain reaction mechanism was verified, therefore, by the use of a modified version of the toluene carrier gas technique.

## 4.2. Development of Empirical Model

The decrease in conversion of residue upon adding 1-methyl naphthalene indicated that the radicals formed by the residue reacted with 1-methyl naphthalene, inhibiting further reaction of the residue. This decrease was a result of reactions similar to (39) as shown below.

$$CH_3^{\bullet} + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2^{\bullet} \qquad (39)$$

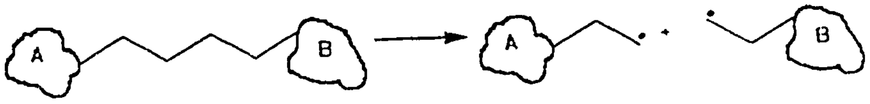
This reaction would be fast in the presence of a large excess of solvent. In the decomposition of the residue, the radicals produced during the initiation step will react to form 1-methyl naphthalene radicals in a fast reaction. These reactions would remove radicals from residue as they are formed and hence slow further decomposition of the residue. These reactions were not 100% efficient at scavenging the radicals and the residue would still decompose, as indicated by the experimental conversions. As in reaction (39), the inhibition of the cracking rate was due to the abstraction of benzylic hydrogen from the 1-methyl naphthalene.

The overall mechanism for residue in 1-methyl naphthalene would follow the reaction scheme developed for n-hexadecane in toluene by Khorasheh and Gray (1993b), reactions (40) - (53) found in Chapter 2. Khorasheh and Gray (1993b) also reported an abundance of benzyl radical derived termination products, thus validating their free radical chain mechanism. Probing the 1-methyl naphthalene experiments for similar termination products helped to verify the role of free radical chain reactions in the decomposition of residue molecules.

From the various model compound studies and complex mixture studies, a free radical chain mechanism can be developed for residue conversion. The use of the toluene carrier gas technique proved that chain mechanisms play an active role in converting residues to lighter products. The review of model compound reactions by Poutsma (1990), suggested the view that a free radical chain model works well if aliphatic carbon was available (beyond methyl substitution).

The initiation step for cracking was assumed to be homolytic breakage of bonds. This step is illustrated below for an aliphatic bridge structure, which has been proven to exist in residues by Strausz (1989). As an alternative, weaker carbon-sulfur bonds in thioether bridges could initiate the radical reactions.

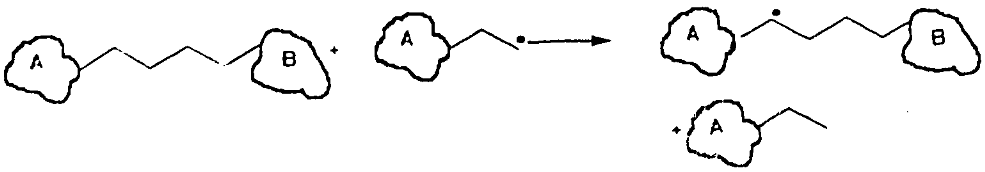
Initiation



(65)

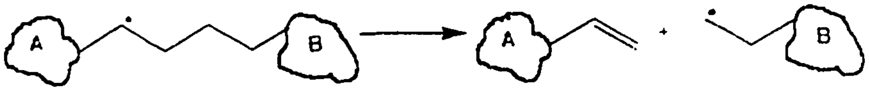
Following Khorasheh's results for n-hexadecane decomposition, the propagation steps for residue conversions are as follows:

### Hydrogen Abstraction

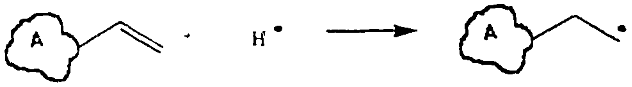

(66)

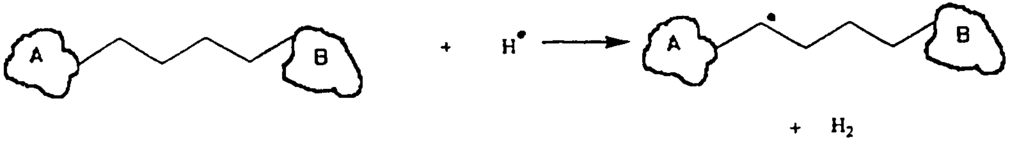

(67)

### β-Scission

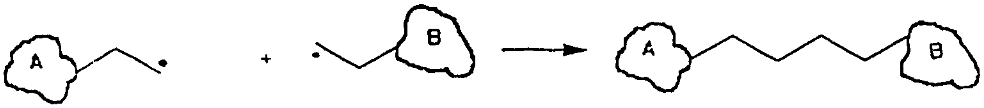

(68)

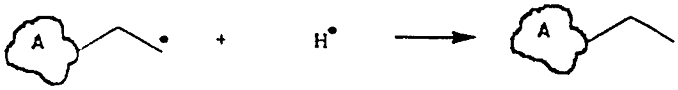
### Hydrogen Radical Reaction


(69)


(70)

### Termination


(71)


(72)

This empirical model for residue hydrocracking was based on various model compound studies and the present work. The various steps in the above mechanism are consistent with results from model compound studies.

## 4.3. Ethylene Addition Experiments

The ethylene blank experiment was performed as described in Chapter 3. The ethylene gas oligomerized to form light liquid products. With an initial pressure of 5.5 MPa, approximately 39 g of liquid product was formed.

The products from experiments with ethylene and nitrogen were distilled using spinning band and D-1160 distillation. The conversions of the residue fractions for both experiments were calculated to account for coke formation. The equations used were as follows. Sample calculations can be found in Appendix C:

$$\text{Residue Conversion} = \frac{\text{Residue in Initial Sample} - (\text{Residue in Product} - \text{Coke Yield} * \text{Residue in Initial Sample})}{\text{Residue in Initial Sample}} \tag{73}$$

$$\text{Coke Yield} = \frac{\text{Solids in Product} - \text{Solids in Feed}}{\text{Residue in Initial Sample}} \tag{74}$$

The conversions of the residue fraction from the ethylene and the nitrogen experiments, taking into account coke formation, were 41.1 % and 57.8 %, respectively. The hydrogen experiments gave a residue conversion of about 48.6 %, but the ethylene and nitrogen experiments were only run for 30 min whereas the hydrogen experiments were run for 1 h. The rate of residue conversion was therefore twice as high in ethylene or nitrogen as in hydrogen.

When the residue fraction was filtered, it was found, following the sample calculations in Appendix C, that the solid content from the products from the ethylene experiments was 0.083 g of solid / g of feed residue whereas the solid content from the products from the nitrogen experiments was 0.037 g of solid / g of feed residue. A summary of the filtration results can be found in Appendix B. The solids remaining after filtering the products from the ethylene experiment were very dark in color, almost black. On the other hand, the solids remaining after filtering the products from the nitrogen experiment were light brown in color similar to the mineral material in the feed bitumen. This observation was expected since the nitrogen experiment did not form as much coke as the ethylene experiment. Using equation (74) on the previous page, only about 0.022 g of coke / g of feed residue was formed for the nitrogen experiments.

The filtered residue fractions and the distillate fractions were analyzed by carbon-13 NMR. The spectra were integrated to determine the amount of carbon in each region. Data for the content of naphthenic, paraffinic and aromatic carbon are listed in Table 4.7. Data for the content of each range in the carbon-13 NMR spectrum (as described in Chapter 3) are shown in Tables 4.8 and Table 4.9. Details of calculations for specific areas and percentages are given in Appendix B. The integration of the carbon-13 NMR spectrum for all fractions was performed using a similar method to ensure that the integration was reliable.

Table 4.7: Concentration of Aromatic, Naphthenic and Paraffinic Carbon from the Carbon-13 NMR Spectra. Note: * This number represents the total aliphatic region since it was difficult to determine paraffinic carbon.

| Sample | $C_{aromatic}$ | $C_{paraffinic}$ | $C_{naphthenic}$ |
|---|---|---|---|
| Ethylene Expt. Distillate | 28.9 | 11.9 | 59.2 |
| Nitrogen Expt. Distillate | 32.4 | 11.7 | 55.9 |
| Ethylene Expt. Residue | 61.5 | 5.8 | 32.7 |
| Nitrogen Expt. Residue | 57.3 | 7.3 | 35.4 |
| Pure Ethylene | 16.1 |  | 83.9* |

Table 4.8: Results for Each Region for the Aliphatic Region of the Carbon-13 NMR Spectra

| Sample | γ-Methyl | β-Methyl | α-Methyl | Methylene | Methyne |
|---|---|---|---|---|---|
| Ethylene Expt. Distillate | 11.2 | 1.9 | 11.8 | 34.2 | 12.0 |
| Nitrogen Expt. Distillate | 7.0 | 2.5 | 12.7 | 34.2 | 11.3 |
| Ethylene Expt. Residue | 4.3 | 1.6 | 5.5 | 20.4 | 6.7 |
| Nitrogen Expt. Residue | 4.1 | 2.0 | 6.5 | 23.3 | 6.9 |
| Pure Ethylene | 15.4 | 5.1 | 14.1 | 42.5 | 6.8 |

Table 4.9: Results for Each Region for the Aromatic Region of the Carbon-13 NMR Spectra

| Sample | $C_{aromatic}$-H | $C_{aromatic}$-C | $C_{aromatic}$-O,N,S |
|---|---|---|---|
| Ethylene Expt. Distillate | 14.9 | 10.2 | 3.8 |
| Nitrogen Expt. Distillate | 15.5 | 11.9 | 4.9 |
| Ethylene Expt. Residue | 36.5 | 18.3 | 6.7 |
| Nitrogen Expt. Residue | 28.9 | 20.6 | 7.7 |
| Pure Ethylene | 6.9 | 5.5 | 3.7 |

The data from the carbon-13 NMR did not provide direct evidence for addition of ethylene to residue radicals, for example, no increase in two-carbon substituents on aromatic rings was observed.

The aromatic region for ethylene experiment was larger than the aromatic region for the nitrogen experiment (especially in $C_{aromatic}$-H region, 100 - 129.5 ppm) as illustrated in Figure 4.2. Ethylene by itself gave a low yield of $C_{aromatic}$, so it would reduce the aromaticity if it were simply reacting in parallel to the cracking of bitumen residue. The increase in the amount of carbon in the aromatic region was not consistent with ethylene reacting with itself and therefore the ethylene must have added to the residue radicals to produce more aromatic rings.

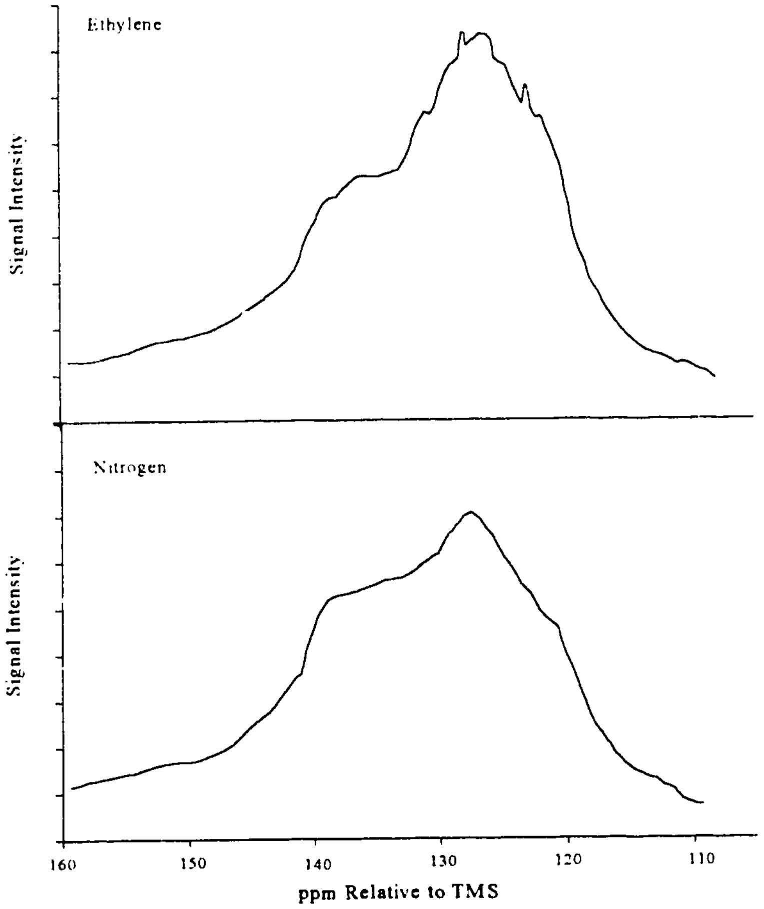


Figure 4.2: Aromatic Region for the Residue Fraction of the Ethylene Gas Experiments and the Nitrogen Gas Experiments, Respectively. The areas under the curves are proportional to the amount of aromatic carbon (61.5 % and 57.3 % respectively). No signal was detected above the baseline in the range 100 - 110 ppm, therefore this range was not shown.

The amount of carbon in the γ-methyl region (11-15 ppm) of the distillate fraction from the experiment reacted under ethylene pressure was higher than for the experiment reacted under nitrogen pressure. The liquid product from ethylene alone had a high concentration of γ-methyl, therefore, ethylene products could account for the increase. A simple additivity calculation was performed as described in Appendix D, assuming that the residue made no contributions to the reaction. Based on this calculation the γ-methyl region should be about 10.8 % of total carbon, but the actual value was 11.2 %. Therefore, most of the increase in the γ-methyl region could be accounted for by ethylene reacting in parallel with the residue.

The coke yield upon adding ethylene to the residue increased 2.2 fold as compared to the control experiment. Ethylene may act as a bridge between two residue molecules, thereby increasing the molecular weight as illustrated in Figure 4.3. Such an increase in molecular weight would promote coke formation.

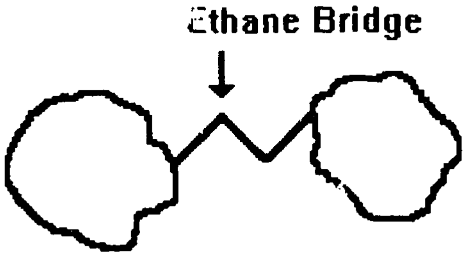


Figure 4.3: Cluster of Two Residue Molecules Bridged by Reaction with Ethylene

Storm et al. (1994, 1995) have indicated that asphaltene colloids have a tendency to flocculate at high temperatures (above 250°C) and that the colloids exist up to temperatures of at least 300°C. These colloids may also exist at 400°C and could be involved in coke formation (Storm, 1996). Storm (1996) suggested that under coking conditions, the quantity of colloids increased due to free radical reactions, eventually leading to the formation of a separate coke phase. In this context, ethylene could serve to bridge colloids into larger particles, thereby aiding in the flocculation of coke.

The addition of ethylene changed the residue composition by increasing the total amount of aromatics present and by increasing the amount of coke formed. These increases were inconsistent with ethylene only reacting in parallel with the residue and therefore, it appeared that ethylene reacted with the residue radicals. However, based on the carbon-13 NMR spectra, ethylene addition reactions were highly non-specific since no pattern for two-carbon addition was found.

## 4.4 Inhibition of Coking through Addition of an Aromatic Solvent

As discussed in Chapter 3, the residue was reacted under a nitrogen atmosphere, with and without the addition of a diluent, to determine the effect of dilution on coke formation. The liquid products from the experiments were filtered to determine the solids content (or coke content). The amount of solids formed in the pure solvent was negligible and was assumed to be only from deposits on the walls of the reactor. Table 4.10 shows the results from filtering the products.

Table 4.10: Solids Formed Based on Amount of Feed Residue for Coking Experiments

| Reaction Type | Number of Repeat Filtrations | Coke Yield g of coke / g of feed residue |
|---|---|---|
| Pure Solvent | 1 | 0.000 |
| Residue in 1-MN | 3 | 0.011 |
| Undiluted Residue | 3 | 0.022 |

Although the amounts of coke formed from the two residue experiments were different, the difference was too small to conclude that the addition of 1-methyl naphthalene gave significant suppression of coke. More experiments at longer reaction times are required to validate the results. The difference in coke formation between the two liquid-phase compositions could be more significant at longer reaction times.

The filtered products were analyzed by GC to determine the amount of termination products derived from 1-methyl naphthalene. This result was used to calculate the ratio of termination products from the residue in 1-methyl naphthalene experiment to the termination products from the pure 1-methyl naphthalene experiment. Similar to the trend in the hydrogen experiments, a 2.1 fold increase in termination products was found (Table 4.11). The hydrogen experiments, however, gave a much larger increase in the concentration of termination products from 1-methvl naphthalene than the nitrogen experiments. For the hydrogen experiments, the amount of termination products found was 1.32 x$10^{-3}$ g of termination product / g of 1-methyl naphthalene, which was 2.7 fold higher than the nitrogen experiment. In addition, the conversion of the residue was much higher under the nitrogen experiment. It was uncertain why there was a difference between the two ratios, but it may be due to the different gases used and the different pressures used for the two experiments.

Table 4 11: Ratio of Termination Products From Residue in 1-Methyl Naphthalene Under Nitrogen Pressure Experiments to Pure 1-Methyl Naphthalene Under Nitrogen Pressure Experiments

| Rxn Number | Termination Products in Sample Mean | Correction for Residue Contribution | Ratio of Residue in 1-MN to Pure 1-MN |
|---|---|---|---|
| Pure 1-MN | 0.241 E-3<br>g/g 1-MN | —— | 2.05 |
| | | 0.493 E-3<br>g/g 1-MN | |
| Residue in 1-MN | 0.709 E-3<br>g/g Mixture | | |
| Correction for Background signal for Residue | | | |
| Undiluted Residue | 0.299 E-3<br>g/g Mixture | | |

The differences found in the coke yield were not significant enough to draw definite conclusions. More data are required to provide validation that the decrease in coke yield was significant. The other result found was an increase in termination products. This increase upon dilution indicated that there was kinetic coupling between 1-methyl naphthalene and the residue radicals.

If coking is a bimolecular process where two residue species react, then dilution should slow down the reaction. Dilution would, therefore, reduce coke yield and increase termination products. Adding a diluent could also change the phase behavior of the residue. Several researchers have suggested that the instability of asphaltenes in solution may lead to coke formation. Andersen and Birdi (1991) and Koots and Speight (1975) reported that the presence of resins within the oil increased the solubility of the asphaltenes and hence decreased the amount of precipitation; however, asphaltene precipitation is not synonymous with coke formation. The primary reason for enhanced stability upon dilution with resins is due to the polar and aromatic nature of the resins.

However, Le Page et al. (1987) found that heavy resins inhibit the cracking of other compounds and have the tendency to polycondense to form heavy molecular weight materials (or coke). The role of resins in suppressing or increasing coke formation is, therefore, unclear at present.

Takatsuka et al. (1988) have developed a ternary composition diagram to predict product stability based on the assumption that asphaltene instability leads to coke formation. This diagram was based on the observation that the best conditions for stability in processing residues was a composition with low saturates, high aromatics, high resins and low asphaltenes. For the experiments performed with 1-methyl naphthalene, there was approximately 85 wt % of aromatics in the mixture. According to Takatsuka et al. (1988), the effect of adding the aromatic diluent would be either no change in coke formation or an increase in coking depending on the specific phase diagram of the residue fraction Based on the literature on phase stability and on the kinetics of the reaction, it is difficult to conclude whether coking under these experimental conditions would be kinetically driven or be due to phase equilibrium.

It may be possible to distinguish between kinetic and phase equilibrium control by performing two other types of experiments. The first experiment that could be performed would be to use perdeuterated 1-methyl naphthalene to enable small angle neutron scattering (SANS) tracing of the reaction. Data from SANS could be used to investigate the structural changes of the asphaltene colloids during coking (Thiyagarajan et al., 1995). An increase in the concentration of asphaltene colloids early in the reaction would support a thermodynamic mechanism governing phase behavior. The second experiment that could help separate the two mechanisms would be to use different solvents and compare the results. For example, removing a methyl group from the 1-methyl naphthalene (i.e. use naphthalene), would reduce the kinetic coupling of the solvent with the residue. The dilution effect would still be present, therefore, varying the dilution ratio of solvent to residue would define the dependence of reaction variables on concentration. Successive dilution would give a monotonic change in coke yield if the reaction is kinetically controlled, whereas phase equilibrium control might give discontinuous changes due to boundaries in phase behavior.

# 5.0 Conclusions and Recommendations for Future Work

## 5.1 Conclusions

1. The residue conversion at 400°C, 1 h reaction time and 13.8 MPa hydrogen pressure without solvent addition was 49 % on average. The conversion of residue was reduced when the 1-methyl naphthalene solvent was added, to 41 % or less.

2. There was a 5.9 fold increase in termination products derived from 1-methyl naphthalene when residue was added to the solvent.

3. The changes in conversion and yield of termination products upon dilution with 1-methyl naphthalene were consistent with a free radical chain mechanism for residue conversion.

4. The reaction of residue under ethylene gave more coke and a more aromatic residue product than the reaction under nitrogen. These changes were consistent with reactions of ethylene with residue radicals to give bridging between molecules and formation of aromatics.

## 5.2 Recommendations for Future Work

1. Approaches to decrease variability on residue conversion in 1-methyl naphthalene:
    - a. Perform experiments with a catalyst. A catalyst would scavenge the oxygen in the reactor and thereby decrease the variability in conversion.
    - b. Use the freeze-thaw method to remove residual oxygen as described by Fabuss et al. (1964).

2. Use a CSTR reactor to reduce the errors inherent in batch reactors.

3. Examine the effect of dilution on coking by performing further experiments.
    - a. Extend the reaction time to obtain higher coke yields from the control sample under nitrogen.
    - b. Use perdeuterated 1-methyl naphthalene for SANS analysis.
    - c. Use naphthalene as well as 1-methyl naphthalene and vary the dilution ratio to determine if there is a systematic difference in coke yield.

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# Appendix A: Experimental Data

Summary of Reactor Runs

| Run Number | Syncrude Tag # | Description |
|---|---|---|
| CAB-1-1 | | Pure 1-Methyl Naphthalene Experiments |
| CAB-4-1 | | Pure 1-Methyl Naphthalene Experiments |
| CAB-5-1 | | Pure 1-Methyl Naphthalene Experiments |
| CAB-6-1 | | Pure 1-Methyl Naphthalene Experiment |
| CAB-7-1 | | Pure 1-Methyl Naphthalene Experiment without Purging the Air within the Reactor |
| CAB-1-2 | 3HPP0119 | Residue in 1-Methyl Naphthalene Experiments |
| CAB-4-2 | 3HPP0133 | Residue in 1-Methyl Naphthalene Experiments |
| CAB-5-2 | 3HPP0134 | Residue in 1-Methyl Naphthalene Experiments |
| CAB-6-2 | 3HPP0136 | Residue in 1-Methyl Naphthalene Experiments |
| CAB-1-3 | 3HPP0118 | Undiluted Residue Experiments |
| CAB-3-3 | 3HPP0125 | Undiluted Residue Experiments |
| CAB-5-3 | 3HPP0135 | Undiluted Residue Experiments |
| CYB-1-1 | | Pure Ethylene Gas Experiment |
| CYB-1-2 | 3HPP0120 | Residue Under Ethylene Gas Pressure |
| CYB-1-3 | 3HPP0121 | Residue Under Nitrogen Gas Pressure |
| CYB-2-1 | | Pure 1-Methyl Naphthalene Under Nitrogen Gas Pressure Experiments |
| CYB-2-2 | | Residue in 1-Methyl Naphthalene Under Nitrogen Gas Pressure Experiments |

Table 7.1: Experiments for Pure 1-Methyl Naphthalene (1-MN) Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure

Reaction #: CAB-1-1 Amount of 1-MN = 225 mL
Purity = 98 %

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 4.8 | 167 | 900 |
| 12 | | 6.2 | 351 | 660 |
| 31 | | 8.3 | 401 | 677 |
| 40 | 0 | 13.8 | 398 | 685 |
| 50 | 10 | 13.6 | 401 | 692 |
| 60 | 20 | 13.8 | 401 | 694 |
| 70 | 30 | 14.0 | 401 | 699 |
| 80 | 40 | 14.1 | 401 | 702 |
| 90 | 50 | 14.1 | 401 | 699 |
| 100 | 60 | 14.1 | 401 | 700 |

Reaction #: CAB-4-1 Amount of 1-MN = 225 mL
Purity = 98 %

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 9.5 | 127 | 653 |
| 30 | | 11.5 | 223 | 657 |
| 105 | | 14.0 | 356 | 659 |
| 147 | 0 | 13.8 | 399 | 660 |
| 177 | 30 | 13.8 | 399 | 660 |
| 207 | 60 | 13.6 | 399 | 660 |

Reaction #: CAB-5-1 Amount of 1-MN = 225 mL
Purity = 95 %

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 7.6 | 23 | 563 |
| 38 | 0 | 13.8 | 398 | 646 |
| 98 | 60 | 13.4 | 401 | 650 |

Reaction #: CAB-6-1 Amount of 1-MN = 225 mL
Purity = 99.1 %

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.9 | 22 | 314 |
| 40 | 0 | 13.4 | 398 | 640 |
| 100 | 60 | 14.8 | 401 | 664 |

Reaction #: CAB-7-1 Amount of 1-MN = 225 mL
Purity = 99.1 %

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| | 0 | 13.8 | 399 | 640 |
| | 60 | 13.8 | 401 | 655 |

Table 7.2 Residue in 1-Methyl Naphthalene Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure - Series 1 (Purity = 98 %)

Reaction #: CAB-1-2-A

Amount of 1-MN = 225 mL
Amount of Bitumen = 40.181 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 5.2 | 24 | 686 |
| 8 | | 6.2 | 89 | 704 |
| 17 | | 6.9 | 177 | 709 |
| 28 | | 8.3 | 290 | 715 |
| 37 | | 9.7 | 376 | 710 |
| 47 | 0 | 13.8 | 399 | 721 |
| 57 | 10 | 13.6 | 400 | 698 |
| 67 | 20 | 13.8 | 401 | 697 |
| 77 | 30 | 13.8 | 401 | 702 |
| 87 | 40 | 13.8 | 401 | 708 |
| 97 | 50 | 13.8 | 401 | 710 |
| 107 | 60 | 13.8 | 401 | 712 |

Reaction #: CAB-1-2-B

Amount of 1-MN = 225 mL
Amount of Bitumen = 55 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 5.9 | 100 | 635 |
| 14 | | 7.2 | 247 | 657 |
| 24 | | 8.6 | 336 | 669 |
| 37 | | 10.0 | 398 | 695 |
| 39 | 0 | 13.4 | 399 | 696 |
| 49 | 10 | 13.4 | 400 | 703 |
| 59 | 20 | 13.4 | 401 | 709 |
| 69 | 30 | 13.4 | 401 | 699 |
| 79 | 40 | 13.4 | 401 | 701 |
| 89 | 50 | 13.4 | 401 | 704 |
| 99 | 60 | 13.1 | 401 | 705 |

Reaction #: CAB-1-2-C

Amount of 1-MN = 225 mL
Amount of Bitumen = 44.99 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 5.5 | 47 | 459 |
| 8 | | 6.4 | 123 | 667 |
| 18 | | 7.6 | 246 | 671 |
| 30 | | 9.3 | 366 | 683 |
| 42 | | 10.0 | 398 | 687 |
| 44 | 0 | 13.8 | 398 | 689 |
| 54 | 10 | 14.1 | 401 | 695 |
| 64 | 20 | 14.3 | 401 | 703 |
| 74 | 30 | 14.3 | 401 | 704 |
| 84 | 40 | 14.3 | 401 | 708 |
| 94 | 50 | 14.3 | 401 | 710 |
| 104 | 60 | 14.3 | 401 | 712 |

Reaction #: CAB-1-2-D

Amount of 1-MN = 225 mL
Amount of Bitumen = 47.01 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 5.9 | 99 | 557 |
| 10 | | 6.9 | 211 | 650 |
| 30 | | 9.7 | 390 | 673 |
| 46 | 0 | 13.4 | 401 | 681 |
| 56 | 10 | 13.6 | 401 | 687 |
| 66 | 20 | 13.8 | 401 | 693 |
| 76 | 30 | 13.8 | 401 | 698 |
| 86 | 40 | 13.8 | 401 | 701 |
| 96 | 50 | 13.8 | 401 | 703 |
| 106 | 60 | 13.8 | 401 | 704 |

Reaction # CAB-1-2-E

Amount of 1-MN = 225 mL
Amount of Bitumen = 45.23 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 5.0 | 20 | 430 |
| 16 | | 6.6 | 150 | 435 |
| 50 | 0 | 13.8 | 398 | 700 |
| 60 | 10 | 14.0 | 401 | 707 |
| 70 | 20 | 14.0 | 401 | 709 |
| 80 | 30 | 14.0 | 401 | 711 |
| 90 | 40 | 14.0 | 401 | 713 |
| 100 | 50 | 14.0 | 401 | 714 |
| 110 | 60 | 14.0 | 401 | 714 |

Table 7.3: Residue in 1-Methyl Naphthalene Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure - Series 4 (Purity = 98 %)

Reaction #: CAB-4-2-A

Amount of 1-MN = 224 mL
Amount of Bitumen = 46.631 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 |  | 9.8 | 210 | 680 |
| 24 | 0 | 13.8 | 398 | 657 |
| 26 | 12 | 14.1 | 401 | 660 |
| 68 | 30 | 14.1 | 401 | 664 |
| 98 | 60 | 14.1 | 401 | 667 |

Reaction #: CAB-4-2-B

Amount of 1-MN = 226 mL
Amount of Bitumen = 45.694 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 |  | 6.6 | 23 | 504 |
| 20 |  | 9.7 | 212 | 515 |
| 30 |  | 11.4 | 328 | 520 |
| 43 | 0 | 13.6 | 398 | 654 |
| 91 | 48 | 14.1 | 401 | 651 |
| 103 | 60 | 14.1 | 401 | 672 |

Reaction #: CAB-4-2-C

Amount of 1-MN = 227 mL
Amount of Bitumen = 44.774 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 |  | 6.4 | 24 | 406 |
| 39 |  | 13.1 | 389 | 636 |
| 47 | 0 | 13.4 | 398 | 654 |
| 107 | 60 | 13.8 | 401 | 661 |

Reaction #: CAB-4-2-D

Amount of 1-MN = 225 mL
Amount of Bitumen = 48.089 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 |  | 6.9 | 22 | 545 |
| 48 | 0 | 13.8 | 398 | 657 |
| 108 | 60 | 14.0 | 400 | 674 |

Reaction # CAB-4-2-E

Amount of 1-MN = 226 mL
Amount of Bitumen = 45.512 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.9 | 23 | 299 |
| 35 | | 12.4 | 354 | 573 |
| 48 | 0 | 14.1 | 398 | 574 |
| 108 | 60 | 14.5 | 401 | 682 |

Table 7.4: Residue in 1-Methyl Naphthalene Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure - Series 5 (Purity = 95 %)

Reaction #: CAB-5-2-A

Amount of 1-MN = 225 mL

Amount of Bitumen = 48.251 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.9 | 34 | 544 |
| 22 | | 10.0 | 239 | 541 |
| 43 | 0 | 13.4 | 397 | 647 |
| 103 | 60 | 14.0 | 401 | 666 |

Reaction #: CAB-5-2-B

Amount of 1-MN = 226 mL

Amount of Bitumen = 45.079 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.6 | 23 | 504 |
| 47 | 0 | 13.8 | 398 | 668 |
| 70 | 23 | 14.3 | 401 | 682 |
| 107 | 60 | 14.1 | 401 | 685 |

Reaction #: CAB-5-2-C

Amount of 1-MN = 228 mL

Amount of Bitumen = 44.424 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.6 | 20 | 445 |
| 44 | 0 | 13.4 | 398 | 645 |
| 104 | 60 | 14.1 | 401 | 682 |

Reaction #: CAB-5-2-D

Amount of 1-MN = 224 mL

Amount of Bitumen = 47.231 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.9 | 45 | 574 |
| 40 | 0 | 13.8 | 398 | 650 |
| 100 | 60 | 13.8 | 401 | 670 |

Reaction #. CAB-5-2-E

Amount of 1-MN = 224 mL
Amount of Bitumen = 45.006 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.6 | 22 | 523 |
| 42 | 0 | 13.6 | 398 | 649 |
| 102 | 60 | 14.3 | 401 | 671 |

Table 7.5: Residue in 1-Methyl Naphthalene Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure - Series 6 (Purity = 99.1 %)

Reaction #: CAB-6-2-A

Amount of 1-MN = 226 mL
Amount of Bitumen = 48.508 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| | 0 | 13.4 | 398 | 648 |
| | 60 | 13.8 | 406 | 651 |

Reaction #: CAB-6-2-B

Amount of 1-MN = 227 mL
Amount of Bitumen = 47.724 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| | 0 | 13.8 | 398 | 653 |
| | 60 | 14.5 | 407 | 657 |

Reaction #: CAB-6-2-C

Amount of 1-MN = 225 mL
Amount of Bitumen = 43.997 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | | | |
| 50 | 0 | 13.8 | 400 | 636 |
| 110 | 60 | 13.8 | 395 | 639 |

Reaction #: CAB-6-2-D

Amount of 1-MN = 227 mL
Amount of Bitumen = 45.533 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| | 0 | 13.8 | 398 | 645 |
| | 60 | 14.3 | 398 | 650 |

Reaction #: CAB-6-2-E Amount of 1-MN = 226 mL
Amount of Bitumen = 45.366 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| | 0 | 13.4 | 399 | 651 |
| | 60 | 14.0 | 406 | 655 |

Table 7.6: Experiments for Undiluted Residue Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure - Series 1

Reaction #: CAB-1-3-A Amount of Bitumen = 126.535 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 8.1 | 179 | 554 |
| 6 | | 9.5 | 248 | 559 |
| 16 | | 10.2 | 353 | 661 |
| 22 | | 10.7 | 411 | 667 |
| 25 | 0 | 14.5 | 410 | 693 |
| 35 | 10 | 14.8 | 389 | 703 |
| 45 | 20 | 14.5 | 407 | 706 |
| 55 | 30 | 14.3 | 395 | 710 |
| 65 | 40 | 14.5 | 401 | 705 |
| 75 | 50 | 14.5 | 401 | 706 |
| 85 | 60 | 14.5 | 401 | 702 |

Reaction #: CAB-1-3-B Amount of Bitumen = 128.292 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 14.5 | 413 | 685 |
| 10 | | 14.7 | 398 | 694 |
| 20 | | 15.5 | 406 | 701 |
| 30 | | 14.0 | 408 | 701 |
| 40 | | 14.0 | 399 | 706 |
| 50 | | 13.8 | 399 | 712 |
| 60 | | 14.0 | 404 | 713 |

Table 7.7 Experiments for Undiluted Residue Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure - Series 3

Reaction # CAB-3-3-A Amount of Bitumen = 127.286 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 7.1 | 25 | 0 |
| 20 | | 8.3 | 64 | 0 |
| 30 | | 8.6 | 86 | 651 |
| 40 | | 9.3 | 99 | 655 |
| 50 | | 10.3 | 165 | 660 |
| 60 | | 10.7 | 190 | 661 |
| 70 | | 11.4 | 214 | 663 |
| 80 | | 11.7 | 236 | 664 |
| 90 | | 12.1 | 256 | 664 |
| 100 | | 13.8 | 350 | 667 |
| 110 | | 14.1 | 362 | 667 |
| 120 | | 14.3 | 371 | 666 |
| 130 | | 14.5 | 379 | 666 |
| 153 | 0 | 13.8 | 399 | 666 |
| 163 | 10 | 13.8 | 400 | 666 |
| 173 | 20 | 13.8 | 392 | 667 |
| 183 | 30 | 13.8 | 398 | 667 |
| 193 | 40 | 13.8 | 402 | 667 |
| 203 | 50 | 13.8 | 392 | 667 |
| 213 | 60 | 13.8 | 396 | 667 |

Reaction #: CAB-3-3-B Amount of Bitumen = 123.96 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 7.2 | 27 | 0 |
| 10 | | 7.4 | 34 | 0 |
| 20 | | 8.3 | 62 | 0 |
| 30 | | 8.8 | 90 | 0 |
| 40 | | 9.3 | 99 | 0 |
| 110 | | 12.8 | 287 | 668 |
| 120 | | 14.5 | 369 | 670 |
| 157 | 0 | 14.1 | 399 | 671 |
| 167 | 10 | 14.1 | 400 | 670 |
| 177 | 20 | 14.0 | 391 | 671 |
| 197 | 40 | 13.8 | 402 | 671 |
| 207 | 50 | 13.8 | 392 | 671 |
| 217 | 60 | 13.8 | 396 | 671 |

Table 7.8: Experiments for Undiluted Residue Reacted for 1 h at 400°C Under 13.8 MPa Hydrogen Pressure - Series 5

Reaction #: CAB-5-3-A Amount of Bitumen = 133.822 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.9 | 21 | 0 |
| 47 | 0 | 13.8 | 400 | 563 |
| 107 | 60 | 14.3 | 401 | 672 |

Reaction #: CAB-5-3-B Amount of Bitumen = 127.639 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 6.9 | 35 | 0 |
| 48 | 0 | 13.8 | 401 | 631 |
| 108 | 60 | 13.8 | 401 | 641 |

Table 7.9: Pure Ethylene Gas Reacted at 400°C for 30 min

Reaction #: CYB-1-1

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 5.5 | 22 | 537 |
| 10 | | 8.0 | 62 | 537 |
| 20 | | 12.1 | 118 | 538 |
| 30 | | 14.5 | 176 | 690 |
| 40 | | 14.5 | 241 | 692 |
| 50 | | 14.5 | 297 | 694 |
| 60 | | 14.1 | 348 | 696 |
| 70 | | 14.1 | 384 | 697 |
| 75 | 0 | 12.4 | 407 | 697 |
| 85 | 10 | 7.8 | 391 | 698 |
| 95 | 20 | 6.7 | 409 | 699 |
| 105 | 30 | 5.5 | 393 | 699 |

Table 7.10. Residue Reacted Under Ethylene Gas Pressure at 400 °C for 30 min

Reaction #: CYB-1-2-A Amount of Bitumen = 127.636 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 |  | 4.8 | 24 | 0.0 |
| 30 |  | 7.6 | 179 | 634 |
| 40 |  | 8.6 | 228 | 635 |
| 50 |  | 9.7 | 278 | 637 |
| 60 |  | 10.7 | 338 | 639 |
| 70 |  | 10.3 | 388 | 641 |
| 75 | 0 | 9.8 | 404 | 641 |
| 85 | 10 | 8.1 | 403 | 642 |
| 95 | 20 | 7.9 | 399 | 643 |
| 105 | 30 | 7.9 | 406 | 643 |

Reaction #: CYB-1-2-B Amount of Bitumen = 126.833 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 |  | 5.2 | 22 | 0.0 |
| 10 |  | 5.7 | 31 | 0.0 |
| 20 |  | 7.2 | 81 | 622 |
| 30 |  | 8.4 | 161 | 623 |
| 40 |  | 10.3 | 260 | 626 |
| 50 |  | 11.9 | 296 | 628 |
| 70 |  | 12.1 | 393 | 641 |
| 75 | 0 | 11.5 | 404 | 679 |
| 85 | 10 | 8.8 | 402 | 391 |
| 95 | 20 | 8.3 | 395 | 682 |
| 105 | 30 | 8.3 | 392 | 683 |

Table 7.11: Residue Reacted Under Nitrogen Gas Pressure at 400°C for 30 min

Reaction #: CYB-1-3-A Amount of Bitumen = 127.227 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 4.1 | 26 | 0.0 |
| 10 | | 4.3 | 34 | 0.0 |
| 20 | | 5.2 | 74 | 553 |
| 30 | | 5.9 | 149 | 635 |
| 40 | | 6.6 | 240 | 639 |
| 50 | | 7.1 | 284 | 640 |
| 60 | | 7.8 | 343 | 342 |
| 70 | | 8.6 | 389 | 643 |
| 75 | 0 | 10.5 | 405 | 696 |
| 85 | 10 | 11.2 | 391 | 697 |
| 95 | 20 | 12.2 | 409 | 699 |
| 105 | 30 | 12.2 | 393 | 699 |

Reaction #: CYB-1-3-B Amount of Bitumen = 125.808 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 4.1 | 24 | 0.0 |
| 10 | | 4.3 | 28 | 0.0 |
| 20 | | 5.2 | 73 | 0.0 |
| 30 | | 5.9 | 156 | 622 |
| 40 | | 6.6 | 242 | 624 |
| 50 | | 7.2 | 306 | 627 |
| 70 | 0 | 10.3 | 400 | 672 |
| 80 | 10 | 10.9 | 409 | 673 |
| 90 | 20 | 11.9 | 390 | 675 |
| 100 | 30 | 12.1 | 409 | 676 |

Table 7.12 Coking Experiment - 1-Methyl Naphthalene Under Nitrogen Pressure at 400°C for 30 min

Reaction #: CYB-2-1 Amount of 1-MN = 225 mL

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 | | 5.2 | 24 | 415 |
| 54 | 0 | 10.3 | 401 | 528 |
| 84 | 30 | 11.0 | 403 | 530 |

Table 7.13 Coking Experiment - Residue in 1-Methyl Naphthalene Under Nitrogen Pressure at 400°C for 30 min

Reaction #: CYB-2-2

Amount of 1-MN = 225 mL

Amount of Bitumen = 44.416 g

| Time (min) | Rxn Time (min) | Pressure (MPa) | Temp (°C) | RPM |
|---|---|---|---|---|
| 0 |  | 4.5 | 27 | 436 |
| 57 | 0 | 10.3 | 398 | 642 |
| 87 | 30 | 11.7 | 401 | 645 |

# Appendix B: Analyzed Data

## 1. Reactor Data

Table 8.1: Data Obtained from Each Reactor Run

| Reaction # | Initial 424°C+ Bitumen (g) | Initial 524°C+ Residue (g) | Initial Reactor Liquid (g) | Total Liquid Product (g) |
|---|---|---|---|---|
| CAB-1-1 | 0 | 0 | 225 | 222.183 |
| CAB-4-1 | 0 | 0 | 225 | 225.355 |
| CAB-5-1 | 0 | 0 | 225 | 213.028 |
| CAB-6-1 | 0 | 0 | 225 | 223.123 |
| CAB-7-1 | 0 | 0 | 225 | 220.953 |
| CAB-1-2 | 232.411 | 158.96 | 1357.411 | 1328.377 |
| CAB-4-2 | 230.7 | 157.80 | 1358.7 | 1330.2 |
| CAB-5-2 | 229.991 | 157.314 | 1356.991 | 1345.49 |
| CAB-6-2 | 231.128 | 158.092 | 1361.128 | 1312.845 |
| CAB-1-3 | 254.827 | 174.3 | 254.827 | 224.047 |
| CAB-3-3 | 251.246 | 171.852 | 251.246 | 205.582 |
| CAB-5-3 | 261.461 | 178.839 | 261.461 | 233.677 |
| CYB-1-1 | 0 | 0 | 0 | 39.047 |
| CYB-1-2 | 254.469 | 174.057 | 254.469 | 287.405 |
| CYB-1-3 | 253.035 | 173.076 | 253.035 | 182.848 |
| CYB-2-1 | 0 | 0 | 216 | 218.488 |
| CYB-2-2 | 46.797 | 32.009 | 273.797 | 265.976 |

## 2. Distillation Data

Table 8.2: Data Obtained from Spinning Band Distillation of Each Sample

| Reaction # | Sample Distilled (g) | IBP - 195°C (g) | 195 - 343°C (g) | 343°C+ (g) |
|---|---|---|---|---|
| CAB-1-2 | 1316.1 | 10.1 | 1103.1 | 191.3 |
| CAB-4-2 | 1107.1 | 10.7 | 933.8 | 175.8 |
| CAB-5-2 | 1063.9 | 11.1 | 897.4 | 133.2 |
| CAB-6-2 | 1019.9 | 4.4 | 866.0 | 130.6 |
| CAB-1-3 | 194.6 | 15.6 | 26.4 | 151.3 |
| CAB-3-3 | 179.7 | 7.8 | 21.6 | 146.2 |
| CAB-5-3 | 204.9 | 10.8 | 28.9 | 161 |
| CYB-1-2 | 268.1 | 37.5 | 33.3 | 191.1 |
| CYB-1-3 | 145.1 | 13.4 | 19.6 | 109.6 |

Table 8.3 Data Obtained from D-1160 Distillation of Each Sample

| Reaction # | Sample Distilled (g) | 343 - 524°C (g) | 524°C+ (g) |
|---|---|---|---|
| CAB-1-2 | 173.6 | 31.3 | 140.82 |
| CAB-4-2 | 132.54 | 57.28 | 72.45 |
| CAB-5-2 | 112.24 | 45.46 | 64.06 |
| CAB-6-2 | 115.16 | 49.49 | 63.25 |
| CAB-1-3 | 138.39 | 66.48 | 68.86 |
| CAB-3-3 | 134.36 | 60.81 | 70.87 |
| CAB-5-3 | 149.61 | 69.63 | 77.34 |
| CYB-1-2 | 168.94 | 70.45 | 94.35 |
| CYB-1-3 | 88.94 | 37.21 | 48.47 |

## 3. Termination Product Data

Table 8.4: GC Data for Termination Product Calculation For 1-Methyl Naphthalene Diluent Experiments

| Rxn Number | Area of Standard | Area of Termination Product | Ratio of Areas | Weight Fraction of Standard | Fraction of Termination Product in Sample |
|---|---|---|---|---|---|
| CAB-1-1-A | 14875 | 19299 | 1.297 | 2.904 E-4 | 0.0003767 |
| CAB-1-1-B | 14246 | 12927 | 0.907 | 2.904 E-4 | 0.0002635 |
| CAB-4-1-A | 43262 | 21818 | 0.504 | 2.589 E-4 | 0.0001306 |
| CAB-4-1-B | 38519 | 18636 | 0.484 | 2.589 E-4 | 0.0001253 |
| CAB-5-1-A | 23834 | 69516 | 2.917 | 3.025 E-4 | 0.0008823 |
| CAB-5-1-B | 21135 | 66161 | 3.130 | 3.025 E-4 | 0.0009469 |
| CAB-1-2-A | 24110 | 87040 | 3.610 | 3.195 E-4 | 0.001153 |
| CAB-1-2-B | 24714 | 101501 | 4.107 | 3.195 E-4 | 0.001312 |
| CAB-4-2-A | 48448 | 281336 | 5.807 | 3.593 E-4 | 0.002086 |
| CAB-4-2-C | 36402 | 198983 | 5.466 | 3.593 E-4 | 0.001964 |
| CAB-5-2-A | 26596 | 302232 | 11.364 | 2.794 E-4 | 0.003175 |
| CAB-5-2-B | 24819 | 81246 | 3.274 | 2.794 E-4 | 0.000917 |
| CAB-5-2-C | 14542 | 2798 | 0.192 | 2.794 E-4 | 0.0000538 |
| CAB-6-2-A | 62782 | 417203 | 6.645 | 3.903 E-4 | 0.00259 |
| CAB-6-2-B | 59269 | 397115 | 6.700 | 3.903 E-4 | 0.00262 |
| CAB-1-3-A | 129900 | 1575017 | 12.125 | 2.003 E-4 | 0.002429 |
| CAB-1-3-C | 140530 | 2096930 | 14.922 | 2.003 E-4 | 0.002989 |
| CAB-3-3-A | 104400 | 1763368 | 16.890 | 1.803 E-4 | 0.00305 |
| CAB-3-3-C | 188410 | 4150100 | 22.027 | 1.803 E-4 | 0.00397 |
| CAB-5-3-A | 203950 | 4048030 | 19.848 | 1.906 E-4 | 0.00378 |
| CAB-5-3-B | 91445 | 1282739 | 14.027 | 1.906 E-4 | 0.00267 |
| CAB-6-1-A | 30204 | 44975 | 1.489 | 3.973 E-4 | 0.00059 |
| CAB-6-1-B | 40315 | 54831 | 1.36 | 3.973 E-4 | 0.00054 |
| CAB-7-1-A | 29065 | 392264 | 13.496 | 3.235 E-4 | 0.00437 |
| CAB-7-1-B | 36160 | 492456 | 13.649 | 3.235 E-4 | 0.00441 |
| CAB-6-2-1-A | 259410 | 619153 | 2.3867 | 4.316 E-4 | 0.00103 |
| CAB-6-2-1-B | 47183 | 207699 | 4.402 | 4.316 E-4 | 0.00190 |
| CAB-6-2-3-A | 54327 | 407087 | 7.49 | 4.477 E-4 | 0.00335 |
| CAB-6-2-3-B | 61060 | 141552 | 2.318 | 4.477 E-4 | 0.00104 |
| CAB-6-2-4-A | 60667 | 431264 | 7.108 | 4.648 E-4 | 0.00330 |
| CAB-6-2-4-B | 71899 | 198317 | 2.758 | 4.648 E-4 | 0.00128 |
| CAB-6-2-5-A | 49567 | 337825 | 6.694 | 3.580 E-4 | 0.00240 |
| CAB-6-2-5-B | 58274 | 807194 | 13.851 | 3.580 E-4 | 0.00496 |

Table 8.5: GC Data for Diphenyl Ethane Fraction Calculation For 1-Methyl Naphthalene Diluent Experiments

| Rxn Number | Area of Standard | Area of Termination Product | Ratio of Area | Weight Fraction of Standard | Fraction of Termination Product in Sample |
|---|---|---|---|---|---|
| CAB-1-1-A | 14875 | 6906 | 0.464 | 2.904 E-4 | 0.0001348 |
| CAB-1-1-B | 14246 | 6441 | 0.452 | 2.904 E-4 | 0.0001313 |
| CAB-4-1-A | 43262 | 8276 | 0.191 | 2.589 E-4 | 0.0000495 |
| CAB-4-1-B | 38519 | 6744 | 0.175 | 2.589 E-4 | 0.0000453 |
| CAB-5-1-A | 23834 | 14309 | 0.600 | 2.794 E-4 | 0.0001677 |
| CAB-5-1-B | 21135 | 14950 | 0.707 | 2.794 E-4 | 0.0001976 |
| CAB-1-2-A | 24110 | 15100 | 0.626 | 3.195 E-4 | 0.0002001 |
| CAB-1-2-B | 24714 | 14430 | 0.584 | 3.195 E-4 | 0.0002057 |
| CAB-4-2-A | 48448 | 48600 | 1.003 | 3.593 E-4 | 0.0003604 |
| CAB-4-2-C | 36402 | 34874 | 0.958 | 3.593 E-4 | 0.0003442 |
| CAB-5-2-A | 26596 | 45218 | 1.700 | 2.794 E-4 | 0.000750 |
| CAB-5-2-B | 28979 | 6985 | 0.241 | 2.794 E-4 | 0.0000674 |
| CAB-5-2-C | 14542 | 2798 | 0.192 | 2.793 E-4 | 0.00000536 |
| CAB-6-2-A | 62782 | 67976 | 1.0827 | 3.903 E-4 | 0.000426 |
| CAB-6-2-B | 59269 | 56188 | 0.948 | 3.903 E-4 | 0.000370 |
| CAB-6-1-A | 30204 | 15251 | 0.504 | 3.973 E-4 | 0.000200 |
| CAB-6-1-B | 40315 | 18023 | 0.447 | 3.973 E-4 | 0.000177 |
| CAB-7-1-A | 29065 | 40915 | 1.407 | 3.235 E-4 | 0.00045 |
| CAB-7-1-B | 36160 | 52268 | 1.445 | 3.235 E-4 | 0.000467 |
| CAB-6-2-1-A | 259410 | 84779 | 0.3268 | 4.316 E-4 | 0.000141 |
| CAB-6-2-1-B | 47185 | 32685 | 0.6927 | 4.316 E-4 | 0.000298 |
| CAB-6-2-3-A | 54327 | 64581 | 1.188 | 4.477 E-4 | 0.000532 |
| CAB-6-2-3-B | 61060 | 33381 | 0.5467 | 4.477 E-4 | 0.000245 |
| CAB-6-2-4-A | 60667 | 65945 | 1.087 | 4.648 E-4 | 0.000505 |
| CAB-6-2-4-B | 71899 | 42845 | 0.5959 | 4.648 E-4 | 0.000277 |
| CAB-6-2-5-A | 49567 | 43790 | 0.8833 | 3.579 E-4 | 0.000316 |
| CAB-6-2-5-B | 58274 | 93864 | 1.6107 | 3.579 E-4 | 0.000577 |

Table 8.6: GC Data for Termination Product Calculation for Coking Experiments

| Rxn Number | Area of Standard | Area of Termination Product | Ratio of Areas | Weight Fraction of Standard | Fraction of Termination Product in Sample |
|---|---|---|---|---|---|
| CYB-2-1-A | 223660 | 227076 | 1.015 | 2.578 E-4 | 0.000262 |
| CYB-2-1-B | 106500 | 90516 | 0.8499 | 2.578 E-4 | 0.000219 |
| CYB-2-2-A | 234360 | 506151 | 2.1597 | 3.311 E-4 | 0.000715 |
| CYB-2-2-B | 267680 | 567967 | 2.1218 | 3.311 E-4 | 0.000703 |
| CYB-1-2-A | 1079900 | 5127280 | 4.7479 | 2.872 E-4 | 0.001363 |
| CYB-1-2-B | 843230 | 6356990 | 7.5388 | 2.872 E-4 | 0.002165 |

## 4. Carbon-13 NMR Analysis Data

Table 8.7: Calculation of Percent Carbon for Product From Pure Ethylene Gas Based on Scan Areas

| **Carbon Region** | **Areas From Scan** | **Fraction of Carbon** |
|---|---|---|
| Overall Spectrum | | |
| Aromatic | 2.300 | 0.1614 |
| Aliphatic | 11.95 | 0.8386 |
| Total | 14.25 | 1 |
| Aliphatic Region | | |
| Gamma | 6.7950 | 0.1535 |
| Beta | 2.2760 | 0.0514 |
| Alpha | 6.2150 | 0.1404 |
| Methylene | 18.825 | 0.4253 |
| Methyne | 3.0050 | 0.0679 |
| Total | 37.116 | 0.8385 |
| Aromatic Region | | |
| $C_{aromatic}$-H | 7.4880 | 0.0688 |
| $C_{aromatic}$ -C | 6.0360 | 0.0554 |
| $C_{aromatic}$ -O,N,S | 4.0480 | 0.0372 |
| Total | 17.572 | 0.1614 |

The overall spectrum was used to obtain the split between the aliphatic and aromatic region.

The Aliphatic region was expanded to show the 0 - 60 ppm and used to calculate the carbon regions within it (therefore areas are different from overall).

The Aromatic region was expanded to show the 100 - 160 ppm region.

The fraction of carbon column indicates the fraction of carbon on a consistent basis between the three spectrum

Table 8.8: Calculation of Percent Carbon for Product From Residue Reacted Under Ethylene Gas Pressure (Distillate Fraction) Based on Scan Areas

| **Carbon Region** | **Areas From Scan** | **Fraction of Carbon** |
|---|---|---|
| Overall Spectrum | | |
| Aromatic | 3.950 | 0.2894 |
| Aliphatic | 9.700 | 0.7106 |
| Total | 13.65 | 1 |
| Aliphatic Region | | |
| Paraffin | 6.164 | 0.1184 |
| Naphthene | | 0.5922 |
| | | |
| Gamma | 5.8580 | 0.1125 |
| Beta | 1.0020 | 0.0193 |
| Alpha | 6.1190 | 0.1175 |
| Methylene | 17.783 | 0.3415 |
| Methyne | 6.2380 | 0.1198 |
| Total | 37.001 | 0.7106 |
| Aromatic Region | | |
| $C_{aromatic}$ -H | 19.147 | 0.1492 |
| $C_{aromatic}$ -C | 13.124 | 0.1022 |
| $C_{aromatic}$ -O,N,S | 4.8750 | 0.0380 |
| Total | 37.146 | 0.2894 |

Table 8.9: Calculation of Percent Carbon for Product From Residue Reacted Under Ethylene Gas Pressure (Residue Fraction) Based on Scan Areas

| **Carbon Region** | **Areas From Scan** | **Fraction of Carbon** |
|---|---|---|
| Overall Spectrum | | |
| Aromatic | 14.55 | 0.6152 |
| Aliphatic | 9.100 | 0.3848 |
| Total | 23.65 | 1 |
| Aliphatic Region | | |
| Paraffin | 2.949 | 0.0578 |
| Naphthene | | 0.3270 |
| | | |
| Gamma | 2.1820 | 0.0428 |
| Beta | 0.8080 | 0.0158 |
| Alpha | 2.8350 | 0.0555 |
| Methylene | 10.417 | 0.2040 |
| Methyne | 3.4070 | 0.0667 |
| Total | 19.649 | 0.3848 |
| Aromatic Region | | |
| $C_{aromatic}$ -H | 36.626 | 0.3655 |
| $C_{aromatic}$ -C | 18.308 | 0.1827 |
| $C_{aromatic}$ -O,N,S | 6.7320 | 0.0672 |
| Total | 61.666 | 0.6152 |

Table 8.10: Calculation of Percent Carbon for Product From Residue Reacted Under Nitrogen Gas Pressure (Distillate Fraction) Based on Scan Areas

| **Carbon Region** | **Areas From Scan** | **Fraction of Carbon** |
|---|---|---|
| Overall Spectrum | | |
| Aromatic | 4.400 | 0.3235 |
| Aliphatic | 9.200 | 0.6765 |
| Total | 13.60 | 1 |
| Aliphatic Region | | |
| Paraffin | 4.029 | 0.1170 |
| Naphthene | | 0.5595 |
| | | |
| Gamma | 2.3950 | 0.0695 |
| Beta | 0.8650 | 0.0251 |
| Alpha | 4.3860 | 0.1273 |
| Methylene | 11.775 | 0.3418 |
| Methyne | 3.8850 | 0.1128 |
| Total | 23.306 | 0.6765 |
| Aromatic Region | | |
| $C_{aromatic}$ -H | 19.605 | 0.1553 |
| $C_{aromatic}$ -C | 15.026 | 0.1190 |
| $C_{aromatic}$ -O,N,S | 6.2070 | 0.0492 |
| Total | 40.838 | 0.3235 |

Table 8.11: Calculation of Percent Carbon for Product From Residue Reacted Under Nitrogen Gas Pressure (Residue Fraction) Based on Scan Areas

| **Carbon Region** | **Areas From Scan** | **Fraction of Carbon** |
|---|---|---|
| Overall Spectrum | | |
| Aromatic | 9.650 | 0.5727 |
| Aliphatic | 7.200 | 0.4273 |
| Total | 16.85 | 1 |
| Aliphatic Region | | |
| Paraffin | 1.909 | 0.0730 |
| Naphthene | | 0.3543 |
| | | |
| Gamma | 1.060 | 0.0405 |
| Beta | 0.532 | 0.0204 |
| Alpha | 1.702 | 0.0651 |
| Methylene | 6.077 | 0.2325 |
| Methyne | 1.797 | 0.0688 |
| Total | 11.168 | 0.4273 |
| Aromatic Region | | |
| $C_{aromatic}$ -H | 26.530 | 0.2893 |
| $C_{aromatic}$ -C | 18.907 | 0.2062 |
| $C_{aromatic}$ -O,N,S | 7.0860 | 0.0772 |
| Total | 52.523 | 0.5727 |

## 5. Percent Solids Data

Table 8.12: Calculated Solids Content for Residue Fractions

| Reaction # | Percent Solids in Residue Fraction g of solid / g of product residue | Percent Solids g of solid / g of feed residue |
|---|---|---|
| FEED | 0.015 | 0.015 |
| CAB-1-2 | 0.030 | 0.030 |
| CAB-4-2 | 0.022 | 0.012 |
| CAB-5-2 | 0.055 | 0.034 |
| CAB-1-3 | 0.029 | 0.014 |
| CAB-3-3 | 0.031 | 0.016 |
| CYB-1-2 | 0.127 (n=3) | 0.083 |
| CYB-1-3 | 0.085 (n=3) | 0.037 |
| CYB-2-1 | 0.0001 g solid / g solvent (n=1) | - |
| CYB-2-2 | 0.00442 g solid / g mixture (n=3) | 0.026 |

Sample calculations for percent solid / gram of feed residue can be found in Appendix C.

## 6. Variability in 1-Methyl Naphthalene Purity from Bottle to Bottle

Table 8.13: Purity of Each 1-Methyl Naphthalene Bottle Used for Series CAB-6-2

| Bottle Number | Purities Determined by GC | Average Purity Per Bottle |
|---|---|---|
| 1 | 99.124, 99.198 | 99.161 |
| 2 | 99.143, 99.001 | 99.072 |
| 3 | 99.003, 99.031 | 99.017 |
| 4 | 98.997, 99.210 | 99.101 |
| 5 | 99.163, 99.041 | 99.102 |

The mean purity of the 1-methyl naphthalene is: 99.090 ± 0.052.

# Appendix C: Sample Calculations

## Determination of Average Difference Between Reacted Residue in Solvent and Pure Reacted Solvent

1. For Total Termination Products

a. Average Weight Fraction of Termination Products in Residue in Solvent (CAB-1-2)
(calculation based on first sample of CAB-1-2)

Area of Standard = 24110
Area of Termination Products = 87040
Weight Fraction of Standard = 3.195E-4 g/g mixture

$$\text{Ratio of Areas} = \frac{Area\ of\ termination}{Area\ of\ standard}$$

$$= \frac{87040}{24110}$$

$$= 3.61$$

$$\text{Weight Fraction of Termination Product} = Ratio\ of\ Areas * weight\ of\ standard$$

$$= 3.61 * 3.195\text{E-4 g/g mixture}$$

$$= 0.00115 \text{ g/g mixture}$$

Weight Fraction of Termination Products for second sample was calculated using the same method.

Average Termination Product Weight Fraction of CAB-1-2

$$= \frac{(1st\ sample + 2nd\ sample)}{2}$$

$$= \frac{(0.00115 + 0.00131)}{2}$$

$$= 0.00123 \text{ g/g mixture}$$

b Mean Weight Fraction of Termination Products for Residue in Solvent
(All average values were calculated using above method)

CAB-1-2 = 0.00123 g/g mixture
CAB-4-2 = 0.00203 g/g mixture

$$\text{Mean Weight Fraction of Termination Products} = \frac{\sum_{i=1}^{2} \text{CAB}-i-2}{2}$$

$$= \frac{0.00123 + 0.00203}{2}$$

= 0.00163 g/g mixture

c Correction for Residue Contribution and Dilution
(only performed on mean weight)

Mean Weight Fraction = 0.00128 g/g mixture
Residue Contribution = 0.17 g residue/g mixture
Fraction of Residue Falling in Term. Prod. Area = 3.148E-3 g/g residue
Dilution Factor = 0.83 g 1-methyl naphthalene/g mixture

Correction for Residue Contribution
= mean weight fraction – residue contribution * fraction of residue falling in area
= 0.00163 - 0.17*0.003148
= 0.00109 g/g mixture

$$\text{Correction for Dilution} = \frac{\textit{corrected value}}{\textit{dilution factor}}$$

$$= \frac{0.00109}{0.83}$$

= 1.319 E-3 g/g 1-methyl naphthalene (1-MN)

d. Average Difference Between Reacted Residue in Solvent and Pure Solvent

Corrected Weight of Residue in Solvent = 1.319 E-3 g/g 1-MN
Weight Fraction of Term. Prod. in Pure Solvent = 2.240E-4 g/g 1-MN

$$\text{Ratio of Termination Products} = \frac{\text{weight fraction from residue in solvent}}{\text{weight fraction from solvent}}$$

$$= \frac{1.319E-3}{2.240E-4}$$

$$= 5.88$$

2. For 2,2'-(1,2-Ethanediyl)Bis-Naphthalene Termination Product

a. Average Weight fraction of Term. Prod. from Residue in Solvent (CAB-1-2)
(calculation based on first sample of CAB-1-2)

Area of Standard = 24110
Area of Termination Products = 15100
Weight Fraction of Standard = 3.195E-4 g/g mixture

$$\text{Ratio of Areas} = \frac{\textit{Area of termination}}{\textit{Area of standard}}$$

$$= \frac{87040}{15100}$$

$$= 0.626$$

Weight Fraction of Term. = *Ratio of Areas * weight* fraction *of standard*

= 0.626 * 3.195E-4 g/g mixture

= 0.000200 g/g mixture

Weight fraction of Termination Product for second sample was calculated using the same method.

Average Weight Fraction of Termination Product for CAB-1-2

$$= \frac{(1st\ sample + 2nd\ sample)}{2}$$

$$= \frac{(0.000200 + 0.000187)}{2}$$

= 0.000193 g/g 1-MN

b. Mean Weight fraction of Termination Products for Residue in Solvent
(All average values were calculated using above method)

CAB-1-2 = 0.000194 g/g 1-MN
CAB-4-2 = 0.000352 g/g 1-MN

$$\text{Mean Weight fraction of Termination Products} = \frac{\sum_{i=1}^{2} \text{CAB} - \text{i} - 2}{2}$$

$$= \frac{0.000194 + 0.000352}{2}$$

= 0.000329 g/g 1-MN

c. Average Difference Between Reacted Residue in Solvent and Pure Solvent

Weight Fraction of Term. Prod. in Residue Solvent = 3.29E-4 g/g 1-MN
Weight Fraction of Term. Prod. in Pure Solvent = 9.02E-5 g/g 1-MN

$$\text{Ratio of Termination Products} = \frac{\text{weight fraction of term. prod. in residue in solvent}}{\text{weight fraction of term prod in pure solvent}}$$

$$= \frac{3.29E-4}{9.02E-5}$$

= 3.64

### Calculation of Residue Conversion When Coke Formation was not Significant

The feed residue from the D-1160 distillation contained 68.4% 524°C+ material. This calculation will be based on CAB-1-2 and CAB-1-3.

1. Conversion for CAB-1-2 (residue in solvent)

   a. Weight percent of 524°C+ material left in CAB-1-2

      Total weight of Feed for spinning band = 1316.1 g
      Weight of 343°C+ fraction = 191.3g
      Total weight of feed for D-1160 = 173.6 g
      Weight of 524°C+ fraction = 140.82 g
      Total Liquid Product (TLP) = 1328.4 g
      Residue in initial sample = 158.96 g

      Using ratios the total weight fraction of the 524°C+ portion was found.

      $$\text{Weight fraction of 524°C+} = \frac{140.82}{173.6} * \frac{191.3}{1316.1}$$

      Weight fraction of 524°C+ = 0.1179

   b. Calculation of Residue in TLP

      $$\text{Residue in Product} = \textit{weight fraction of } 524°C + * \, TLP$$

      $$= 0.1179 * 1328.4$$

      $$= 156.61$$

   c. Calculation of conversion

      $$\text{Conversion} = \frac{\textit{residue in initial sample - residue in product}}{\textit{residue in initial sample}}$$

      $$\text{Conversion} = \frac{158.96 - 156.61}{158.96}$$

      Conversion = 1.5 %

2. Conversion of CAB-1-3 (residue)

a. Weight percent of 524°C+ material left in CAB-1-3

Total weight of Feed for spinning band = 194.6 g
Weight of 343°C+ fraction = 151.3 g
Total weight of feed for D-1160 = 138.4 g
Weight of 524°C+ fraction = 68.86 g
TLP = 224.1 g
Residue in initial sample = 174.3 g

Using ratios the total weight fraction of the 524°C+ portion was found.

$$\text{Weight fraction of } 524°\text{C+} = \frac{68.86}{138.4} * \frac{151.3}{194.6}$$

Weight fraction of 524°C+ = 0.387

b. Calculation of Residue in TLP

$$\text{Residue in Product} = \textit{weight fraction of } 524°C + * \textit{TLP}$$

$$= 0.387 * 224.1$$

$$= 86.73$$

c. Calculation of conversion

$$\text{Conversion} = \frac{\textit{residue in initial sample - residue in product}}{\textit{residue in initial sample}}$$

$$\text{Conversion} = \frac{174.3 - 86.73}{174.3}$$

Conversion = 50.3 %

## Determination of Percent Solids based on Feed Residue

This calculation will be based on CAB-1-2.

Gram of solid / gram of product residue = 0.03
Distillation Data from D-1160: Weight of 524°C+ fraction = 140.82 g
Weight of 343°C+ fraction = 173.60 g
Distillation Data from Spinning Band: Weight of 343°C+ fraction = 191.3 g
Weight of total Product = 1316.1 g
Amount of total product collected = 1328.377 g
Amount of 524°C+ material in the feed = 158.96 g

$$\text{Solid Content} = 0.03 * \left(\frac{140.82}{173.60}\right) * \left(\frac{191.30}{1316.1}\right) * \left(\frac{1328.377}{158.96}\right)$$

$$\text{Solid Content} = 0.0299 \text{ g of solid } / \text{ g of feed residue}$$

## Calculation of Residue Conversion When Coke Formation was Significant

The feed residue from the D-1160 distillation contained 68.4% 524°C+ material. This calculation will be based on CYB-1-2.

1. Conversion for CYB-1-2 (residue under ethylene pressure)

a. Weight fraction of 524°C+ material left in CYB-1-2

Total weight of Feed for spinning band = 268.1 g
Weight of 343°C+ fraction = 191.1 g
Total weight of feed for D-1160 = 168.94 g
Weight of 524°C+ fraction = 94.35 g
Total Liquid Product (TLP) = 287.4 g
Residue in initial sample = 174.1 g

Using ratios the total weight fraction of the 524°C+ portion was found.

$$\text{Weight fraction of } 524°\text{C+} = \frac{94.35}{168.94} * \frac{191.1}{268.1}$$

$$\text{Weight fraction of } 524°\text{C+} = 0.398$$

b. Calculation of Residue in TLP

$$\text{Residue in Product} = \textit{weight fraction of } 524^{\circ}C+ * \textit{TLP}$$

$$= 0.398 * 287.4$$

$$= 114.41 \text{ g}$$

c. Calculation of Coke Yield

$$\text{Coke Yield} = \frac{\textit{final solids - initial solids}}{\textit{residue in initial sample}}$$

$$= 0.083 - 0.015$$
$$= 0.068 \text{ g coke / g feed residue}$$

d. Calculation of conversion

$$\text{Conversion} = \frac{\textit{residue in initial sample - (residue in product - coke formed)}}{\textit{residue in initial sample}}$$

$$\text{Conversion} = \frac{174.1 - (114.4 - 0.068 * 174.1)}{174.1}$$

Conversion = 41.1 %

# Appendix D

## Additivity Calculation for the γ-Methyl Region based on Distillate Fractions of Ethylene and Nitrogen Experiment

Assumptions: No interaction of residue with the ethylene. Therefore, the γ-methyl region of the distillate fraction for residue under ethylene pressure would simply be the addition of the nitrogen experiment and the ethylene gas experiment.

Assumed approximately 85 % carbon in the nitrogen distillate fraction (based on Gray, 1994).

Assumed approximately 90 % carbon in the ethylene total liquid product.

a) amount of carbon in each fraction:

TLP formed from the ethylene = 78 g
TLP formed from the nitrogen distillate = 100 g

Carbon in nitrogen distillate = 100*0.85
= 85 g

Carbon in ethylene = 78*0.9
= 70.2 g

b) Assuming no interaction:

Distillate (ethylene + residue) = Distillate (nitrogen + residue) + TLP (ethylene blank)

Therefore, the γ-methyl region can be calculated based on the above assumption.

γ-methyl region for nitrogen distillate = 0.0695
γ-methyl region for ethylene TLP = 0.1535
total carbon present = 155.2

Predicted γ-methyl region for ethylene distillate

$$= \frac{(\gamma\text{-methyl region for nitrogen distillate*amount of carbon} + (\gamma\text{-methyl region for ethylene TLP*amount of carbon }))}{\text{total carbon present}}$$

$$= \frac{(0.0695*85)*(0.1535*70.2)}{155.2}$$

= 0.1075 γ-methyl fraction / total carbon present

The predicted γ-methyl region for ethylene distillate is 10.75 %. Experimentally, this was found to be 11.25 %. Therefore, the increase in the γ-methyl region for ethylene distillate was due to the ethylene reacting in parallel with the residue