ULTRAPYROLYSIS OF n—HEXADECANE IN A NOVEL MICRO—REACTOR

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled,

"ULTRAPYROLYSIS OF n-HEXADECANE IN A NOVEL MICRO-REACTOR"

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ABSTRACT

Hydrocarbon pyrolysis is economically one of the most important industrial reactions. A wide spectrum of feedstocks, ranging from ethane to vacuum gas oils, are pyrolysed to produce olefins vital to the petrochemical industry. In fact, ethylene, the major product, is the base stock for 30% of all petrochemicals produced. Pyrolysis has also been applied to the upgrading of bitumens/heavy oils. At present, in excess of 200,000 barrels per day of upgraded oil are produced at the northern Alberta oil sand plants.

As the economics of pyrolysis operations strongly depend on the feedstock cost, improvements in the selectivity are particularly advantageous. A fast pyrolysis process known as Ultrapyrolysis has made great strides in this regard. By pyrolysing under conditions of short residence times, high temperatures, high heating rates and rapid quenching of the products; ethylene yields have been commercially increased by approximately 11 wt% over that possible with conventional operation. However, the kinetics and reaction mechanism of pyrolysis under these conditions have rarely been studied. Consequently, the Ultrapyrolysis of n—hexadecane, a gas oil model compound, has been chosen for study.

An automated micro—reaction system characterized by a near ideal reaction temperature—time profile has been employed to pyrolyse n—hexadecane. This system employs a Curie point pyrolyser to rapidly heat microgram samples to high temperatures (greater than 600° C) in less than 100 milliseconds. The Curie point phenomenon ensures that a reproducible and perfectly stable temperature is
attained. A rapid direct quench system has been employed to stop the reactions and flush the products into a sophisticated gas chromatography system for direct analysis.

n—Hexadecane has been pyrolysed over conditions which overlap the conventional and Ultrapyrolysis regimes, specifically at 576 to 842°C and 100 to 3200 ms. As noted by previous researchers, the primary products were C_2 to C_{15} 1—olefins, in particular ethylene, as well as methane through propane. The yields of these products, with the exception of ethylene, decreased at higher conversions due to the secondary formation of diolefins, cyclic olefins, aromatics, methane and hydrogen. Peak ethylene production (28 wt%) was exhibited at ultrapyrolytic conditions of 842°C and 500 ms. Experiments with both metal and inert gold—plated heating surfaces have indicated no evidence of catalysis by the hot metal.

A global first order rate expression was derived from the experimental n—hexadecane pyrolysis data. This relation clearly illustrated that the reaction barely developed at 576°C but rapidly proceeded to near completion at 842°C. The predicted activation energy of 39.4 kcal/mol is substantially lower than the reported value of approximately 57 kcal/mol. A similar disparity was noted by Rastogi, who employed the same reaction system to pyrolyse propane. It has been concluded that poor reaction temperature and time control on the part of previous researchers is the cause. In particular, inadequate quenching likely encouraged reactions to proceed longer than intended, thus yielding higher conversions and larger rate constants, particularly at elevated temperatures. Consequently, the activation energy predicted was far higher than that attained in the current study.
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NOMENCLATURE

A  reactor cross-sectional area, m$^2$
chromatographic peak area

$A_0$ frequency factor of the Arrhenius equation, s$^{-1}$

$E_a$ activation energy, cal/mole

F Bessel function, employed in equation (2.3)

$h_3$ outside convective film coefficient, W/(m$^2$ K)

H magnetic field strength, Oe

k first order rate constant, s$^{-1}$
thermal conductivity of n-hexadecane, W/(m K)

$k_g$ thermal conductivity of Pyrex glass, W/(m K)

K amplifier gain

N ferromagnetic wire power consumption per unit surface, W/m$^2$

r radius, m

$r_1$ ferromagnetic wire radius, m

$r_2$ micro-reactor inner wall radius, m

$r_3$ micro-reactor outer wall radius, m

R universal gas constant, 1.987 cal/(mol K)

RF mass response factor

s skin depth of the induced current, m

t time, s

$t_r$ reaction (residence) time, s

$t_r'$ equivalent reaction time, s

T temperature, K
\( T_r \) reference temperature used in the equivalent reactor volume concept, K

\( T_s \) ferromagnetic wire surface temperature, K

\( T_\infty \) resistance heater temperature, K

TRT temperature-rise-time for ferromagnetic wire heating, s

\( U_2 \) overall heat transfer coefficient, W/(m\(^2\) K)

\( V \) reactor volume, m\(^3\)

\( V_e \) equivalent reactor volume, m\(^3\)

\( w_t \) sample weight employed in gas chromatograph calibration, \( \mu \)g

\( x \) fractional conversion

\( z \) reactor length, m

\( a \) thermal diffusivity of n–hexadecane, m\(^2\)/s

\( \gamma \) oscillator frequency, Hz

\( \epsilon \) emissivity

\( \mu_0 \) permeability of free space, \( 4\pi \cdot 10^{-7} \) V s/(A m)

\( \mu_r \) relative magnetic permeability

\( \nu \) number of moles of product per mole of feedstock pyrolysed

\( \rho \) specific electrical resistance of the ferromagnetic wire, \( \Omega \cdot \)m

\( \tau \) space time, s

\( v \) volumetric flow rate, m\(^3\)/s

\( v_o \) inlet volumetric flow rate, m\(^3\)/s
CHAPTER 1 – INTRODUCTION

Hydrocarbon pyrolysis (thermal decomposition under non-catalytic and oxygen-deficient conditions) has long been a reaction of commercial importance. For years, pyrolysis, also termed thermal cracking, has been implemented in refineries as a primary method of producing gasoline from petroleum. More recently, the process has been applied to the upgrading of bitumens/heavy oils. The coking units present at the northern Alberta oil sands plants are transforming very heavy and viscous oils into a product similar to conventional crude.

More important, though, is the application of hydrocarbon pyrolysis for the production of olefins, the basic feedstocks for the petrochemical industry. Economically, this has been one of the most important reactions used industrially since the mid-1950's. Various feedstocks have been employed to meet demand. Canada and the United States have been fortunate to possess abundant natural gas reserves; thus most plants are usually ethane- or propane-based. In contrast, Europe and Japan, have traditionally relied on naphtha as a feedstock. However, in view of the predicted limited future supply of light feedstocks, producers have begun to shift to feedstocks of gas oil, residual oil and even the whole crude itself.

Feedstock cost represents a large portion of the total cost in either olefin production or bitumen upgrading applications. Therefore, the improvement of reaction selectivity has been the object of continuous research and development, dating from initial investigations which were conducted over one hundred years ago. In particular, there is now considerable evidence that the economics of olefin
production can be greatly improved by moving to a fast pyrolysis process known as Ultrapyrolysis. Basically, Ultrapyrolysis entails pyrolysing under conditions of very short residence (reaction) times (less than 500 ms), high temperatures (700 to 1100°C), rapid heating rates (greater than 1000°C/s) and rapid quenching (tens of milliseconds) of the products (Graham et al., 1984). Commercial application of this technology has resulted in ethylene yield increases of approximately 11 wt% over that attainable with conventional pyrolysis processes (Dluzniewski et al., 1981). Overall feed conversion is not increased; rather, the pyrolysis selectivity has been improved. Application of this technology to bitumen upgrading could result in improved liquid yields at the expense of low value by-products such as off-gas and coke.

Unfortunately, an understanding of the scientific fundamentals of hydrocarbon pyrolysis has lagged significantly behind the immense technological advancements, despite considerable work in the field. The cause of this dilemma lies with the nature of the reactions. The pyrolysis of hydrocarbons proceeds through a complex reaction network, involving both radical and molecular schemes and many components. The complexity escalates when the conversion level and, particularly, the molecular weight of the feedstock are increased. Due to this fact, most of the experimental work to date has been devoted to studies of the pyrolysis of low molecular weight paraffins (butane and lighter). The kinetics and reaction mechanism of pyrolysis of these light hydrocarbons is now well established and thus attention has shifted to the pyrolysis of heavier feeds, in keeping with the gradual shift in feedstock.

The past decade has seen a proliferation of publications concerning the
kinetics of heavy hydrocarbon pyrolysis. However, the majority of the studies have been conducted at operating conditions outside the Ultrapyrolysis regime. Temperatures below 600°C are commonly employed and reaction times are usually in the order of seconds, rather than milliseconds. As well, little attention has been paid towards accurate measurement and control of the reaction time and temperature, essential for valid kinetic data. Thus, a real need exists for good kinetic data of heavy hydrocarbon pyrolysis, particularly in the Ultrapyrolysis regime.
CHAPTER 2 – LITERATURE SURVEY

Before a kinetic study of heavy hydrocarbon pyrolysis can be initiated, a good understanding of the industrial and, especially, the theoretical aspects of hydrocarbon pyrolysis must be acquired.

2.1 INDUSTRIAL PYROLYSIS

In conventional hydrocarbon pyrolysis, the feed is mixed with steam and then pyrolysed in a series of multi–tube furnaces. A large excess of steam is employed to lower the partial pressure of the hydrocarbon feed, thus improving the selectivity to olefins. The steam also minimizes coke formation on the reactor tube walls. The residence time of the hydrocarbon–steam mixture is in the order of 350 to 800 ms, while the reaction temperature ranges from 600°C, at the inlet to the radiant section of the furnace, to 830 – 870°C at the outlet (Froment, 1981). Pressures are just above atmospheric (inlet – 3 atm; outlet – 1.8 atm). The pyrolysis products, upon exiting the furnace, enter a multi–tubular heat exchanger, referred to as a transfer line exchanger (TLX), where they are rapidly quenched to 600°C in under 15 ms (Nighswander et al., 1988) and then further cooled to 350°C before flowing to a primary fractionator (Froment, 1981). Feedstock conversions are typically near 100%, with ethylene being the major product.

Over the past decade, dramatic improvements in pyrolysis technology have occurred. Through advancements in tube metallurgy, M.W. Kellogg Co. (Houston, Texas) have been able to pyrolyse a wide variety of feeds, from ethane to vacuum
gas oil, at very high temperatures (greater than 760°C) and very short residence times (less than 100 ms) (Leftin et al., 1976). Significant increases in the ethylene yield have resulted, at the expense of undesirable products such as off-gases (hydrogen and methane) and highly aromatic heavy fuel oil. However, coke build-up in the tubes, typical of conventional steam pyrolysis, still plagues this process.

As a result, several new olefin processes, also operating at short reaction times (less than 300 ms) and high temperatures (greater than 800°C), but based on fast fluidized bed reactor configurations, are being developed. Typically, these processes are also concerned with the rapid heating of the feed and quenching of the products. Thus, they fall under the general heading of Ultrapyrolysis processes. Technologies such as the Ube process (Ube Industries, Ltd.; Japan) and the Thermal Regenerative Cracker (Gulf Oil, Stone & Webster; USA), amongst others, have been successful and are currently nearing commercial application.

Discussion thus far has been limited to hydrocarbon pyrolysis as a means of producing olefins. However, as noted earlier, hydrocarbon pyrolysis is also employed to upgrade heavy oils/bitumens to a less viscous product typical of conventional crude. Fluid coking units, with operating temperatures of 480–560°C and residence times in the order of 2 minutes, are typically employed (Bartholic, 1984). Although substantial upgrading of the feed is accomplished, a considerable portion of this feed is, in fact, converted to low value by-products such as off-gas (hydrogen/methane) and contaminant-laden (sulfur, nitrogen and metals) coke. Improved liquid yields could be obtained through application of ultrapyrolytic technology. In fact, the Engelhard Minerals and Chemicals Corporation. (New
Jersey) has recently introduced the Asphalt Residual Treating (ART) process which claims to upgrade heavy feeds by high temperature (greater than 525°C), short contact time (less than 2 seconds) pyrolysis in a fast fluidized bed (Bartholic, 1984). Effectively, this process vaporizes the lighter, high-hydrogen content portion of the feed with little or no conversion and converts the high-boiling, low-hydrogen content fraction into lighter liquid products, usable coke and gas. The ART process is more than an idea; it has been proven in commercial test units ranging from 7000 to 55000 barrels/day (Logwinuk and Sloan, 1985). Although the operating conditions of the ART process are not quite in the ultrapyrolytic regime, operation at even shorter contact times (less than 500 milliseconds), and presumably higher temperatures, is the long-term goal for this promising technology.

2.2 LABORATORY REACTORS FOR PYROLYSIS STUDIES

The proper design of commercial reactors requires a suitable expression for the intrinsic rate of the pyrolysis reactions. As intrinsic rate equations cannot yet be predicted, experimental data is required. This data is best obtained from a bench-scale laboratory reactor, rather than from a pilot plant or commercial-scale reactor. The reason for this is that with a laboratory reactor, the construction and operating conditions can be chosen to reduce or eliminate the effects of mass and heat transfer, contaminants and catalytic reactor surfaces from the observed measurements. Thus, an accurate equation for the intrinsic rate can be obtained from the experimental data. As well, it is most advantageous if the laboratory reactor is operated isothermally (in space and time), because then temperature may be considered as an independent variable. Otherwise, the treatment of the kinetic data to obtain the reaction rates, is subject to much more uncertainty. Ideally,
pressures should be kept constant as well. However, in pyrolysis studies, an increase in pressure frequently accompanies the reaction; an increase in the total number of moles is the cause. This effect must be taken into account when analyzing the reaction data.

Several different laboratory reactor types are available. However, two general types have been used for determining the rate of hydrocarbon pyrolysis: batch and flow systems. In recent years, shock tube reactors have also been employed. An understanding of the merits and limitations of each will aid in the evaluation of reported kinetic data.

2.2.1 Batch Reactors

Before the 1970's, most laboratory gas-phase pyrolyses of hydrocarbons were carried out in batch reactors. They are seldom employed, however, on a commercial scale as very little product can be produced in a reasonably sized reactor.

In a batch reactor, the reactant is placed in a closed reaction vessel and pyrolysed under constant volume conditions. A series of runs are made at varying lengths of time, after which the reactor is "opened" to permit quantification and analysis of the products. The reaction vessel is usually constructed of high-temperature glasses, such as pyrex or quartz, or, alternatively, metals such as stainless steel or nickel. Gold-plating has often been employed whenever a positively inert reactor surface was deemed necessary. Temperature is maintained constant by means of an electric furnace or a liquid thermostat. As well, batch reactors are generally fairly large, so as to permit a sizable sample and also to
minimize reactor surface effects; a few hundred millilitres is a common size (Mulcahy, 1973).

Unfortunately, many past pyrolysis studies have employed batch reactors that do not meet the ideal laboratory reactor criteria. The large size of many of these reactors has lead to the existence of dead spaces and, in particular, a non-uniform temperature throughout the reactor. Thus, very few have, in fact, been operated isothermally. Despite efforts to minimize the wall effects, many of the studies have been plagued by unwanted reactions caused by the reactor surfaces. As well, some misleading results have been traced back to oxidation reactions stemming from air trapped with the hydrocarbon in the reactor or, even, dissolved in it. To eliminate this effect, the hydrocarbon in the reactor may be alternatively frozen and thawed under vacuum. Otherwise, the hydrocarbon may be flushed with an inert gas into the vessel and the reactor closed under inert gas pressure. However, despite these problems, the batch reactor does have a definite advantage over other reactor types. Since all the reactant being studied is present in the reactor for the same length of time, the reaction time is accurately known.

Even if the above problems are resolved, the intrinsic rates which can be measured accurately by most batch experiments correspond to half-lives (time required for 50% of the reactant to decompose) of between 15 minutes and 100 hours (Fabuss et al., 1964). A half-life of 15 minutes corresponds to a very slow reaction with a first order reaction rate constant of $0.77 \cdot 10^{-3} \text{ s}^{-1}$. For faster reactions, the time required to heat the sample up to reaction temperature and then cool it down becomes an appreciable fraction of the total, and thus the accuracy with which data can be obtained becomes progressively poorer. If, however, the temperature history
is well-defined, the non-isothermal data can be corrected using the equivalent reaction time concept, originally proposed by Hougen and Watson (1947). However, this is a merely a "fix-up" technique; data manipulated using this approach are nowhere near as accurate as true isothermal data. More details on this concept will be given in Section 2.2.4.

2.2.2 Flow Reactors

For reaction times faster than those that can be accurately studied by batch reactors, it is necessary to use a flow system. Thus, especially since the 1970's, tubular-flow reactors have predominantly been employed as laboratory reactors for pyrolysis studies. The added benefit of using this type of reactor is that almost all commercial pyrolysis units are of the same reactor type, namely large scale multi-tube reactors.

In a tubular reactor, there is a continuous flow of reactants in and products out of a cylindrical pipe. This pipe, like the batch reactor, is usually constructed of metals, such as stainless steel, or high-temperature glasses, such as quartz. In some cases, the inner wall has been gold-plated as surface effects are also a problem in tubular-flow reactor studies. Heat is supplied by a furnace encased around the reactor; the temperature of the wall is maintained constant. The reactor is operated at steady-state, thus temperature and composition may vary with position in the reactor but not with time. In an ideal tubular-flow reactor, highly turbulent flow will ensure that there is no mixing in the direction of flow and complete mixing in the radial direction. Thus, concentrations and temperatures will only vary in the axial direction. Consequently, the rate of reaction will vary with reactor length. In
order to obtain kinetic data, a series of runs is normally conducted by varying the feed rate, and thus the residence time, at constant wall temperature. Subsequent runs at different temperatures are then made to establish the activation energy.

The main question connected with the use of the tubular—flow reactor deals with the deviations from ideality. In the laboratory, it is very difficult to realize plug flow, as the Reynolds number is generally less than 100 (Côme, 1983) and, thus, the gas flow is laminar, with a parabolic profile. As a result, mixing in the radial direction will be poor and the temperature will vary across the cross-section due to imperfect radial heat transfer. This condition is most severe at the entrance and exit regions of the reactor; the reacting gas will pass some distance into the reactor before reaching the wall temperature. As well, it will proceed some distance out of the reactor before sufficient cooling stops the reaction. Thermal equilibrium can be greatly accelerated by preheating the reactant. However, significant reaction can occur during the latter stages of preheating; thus, a number of techniques have been employed to make the preheat period as short as possible. Rapid preheat can be achieved by quickly mixing the reactant with a large excess of a hot inert gas, which acts as the heat transfer medium. On several occasions (Depeyre et al., 1985; Kumar and Kunzru, 1985; Blouri et al. 1981), hydrocarbons have been pyrolysed in the presence of steam, thus simulating commercial practice.

Despite all of the above modifications to the tubular—flow reactor operation, it is inevitable that temperature gradients will still occur. The fact that pyrolysis reactions are highly endothermic only makes matters worse. Under rapid reaction conditions, it is difficult to minimize the temperature difference between the reactor wall and the reacting gas. Thus, the tubular—flow reactor diameter should be made
as small, and the flow as high, as possible, so that nearly plug flow and thus isothermal conditions may exist.

Several examples can be given to indicate the experimental conditions under which pyrolysis intrinsic rates can be measured accurately, without appreciable heat transfer limitations. In studies with n-hexadecane (Fabuss et al., 1962) in a 3.2 mm inside diameter by 1.2 m long reactor, the average difference between the reacting gas and the wall temperature (593°C) was estimated to be about 33°C, when the uncorrected first order rate constant was 0.06 s⁻¹. However, when the reaction rate was increased to 0.54 s⁻¹ by increasing the wall temperature to 704°C, the resulting difference between the gas and wall temperature was a substantial 94°C. Residence times varied between 0.25 and 10 s. On the other hand, in a 1 mm inside diameter tubular reactor with residence times of 1 minute, rate constants of up to 0.5 s⁻¹ were obtained with no significant temperature difference between the gas and wall (Sandler and Chung, 1961). The benefits of decreasing the reactor diameter even further were demonstrated by Hepp et al. (1949). They were able to measure ethane pyrolysis rate constants as high as 300 s⁻¹ with fair accuracy by using very high linear flow rates in a 0.8 mm inside diameter by 0.3–0.6 m long reactor. These rapid flow rates corresponded to residence times of about 10 ms; the wall temperature was 1088°C.

It is very clear, from the above discussion, that in all but the smallest diameter reactors, heat transfer limitations exist for pyrolysis reactions above 600°C. One characteristic of rate constants determined under heat-transfer limited conditions is that the apparent activation energy will be substantially less than the 60 ± 5 kcal/mol usually observed for hydrocarbon pyrolysis. As well, the activation
energy will tend to decrease with increased temperature.

If it is necessary to use a reactor of larger than optimum diameter and if the temperature variation as a function of distance through the reactor can be predicted, the equivalent reactor volume concept (Hougen and Watson, 1947) can be applied to convert the data to a pseudo–isothermal basis. This approach is not recommended, though, for reasons to be discussed in Section 2.2.4.

The use of tubular–flow reactors has other complications. Since a velocity gradient exists between the center axis and the wall, there may be an appreciable residence time distribution for the molecules entering the reactor. However, if the length/diameter ratio of the reactor is large enough, plug flow is approximated and the residence time can be calculated to a fair degree of accuracy. However, it is still dependent upon the increase in volume of the reacting mixture with conversion. Consequently, determination of the residence time in a tubular–flow reactor is not a simple matter.

2.2.3 Shock Tube Reactors

In recent years, the specialized experimental technique of the continuous–flow shock reactor has been applied to measure very rapid reaction rates. This reactor type has been ably described by Côme (1983). Reaction times from about 20 ms down to a fraction of a millisecond can be achieved as the reaction technique provides an almost instantaneous change to reaction conditions. The corresponding rate constants are in the order of $0.1 - 200 \text{ s}^{-1}$ (Fabuss et al., 1964). However, due to the complexity of this reactor, it is difficult to accurately
determine the reaction temperature and time (Côme, 1983). Consequently, shock tube reactors are not, in fact, ideal for kinetic studies.

2.2.4 Equivalent Reactor Volume/Reaction Time Concepts

As extensively discussed in the previous sections, it is very difficult to operate isothermally in both tubular–flow and batch reactors. Consequently, correction techniques have been developed. Hougen and Watson (1947) first introduced the equivalent reactor volume and reaction time concepts to account for slight temperature differences in flow and batch reactors, respectively. Froment et al. (1961) further refined the equivalent reactor volume concept. Since then, this concept has been applied to many pyrolysis studies employing tubular–flow reactors.

According to Hougen and Watson, the equivalent reactor volume, $V_e'$, is defined as that volume which, at a constant reference temperature $T_r$, would give the same conversion, $x$, as the actual non–isothermal tubular reactor. The reference temperature has frequently been taken as the arithmetic mean of the process gas temperatures in the last 40% of the reactor (Van Damme et al., 1975). Assuming the pyrolysis reaction is first order, the equivalent reactor volume can be expressed by the following equation:

$$V_e' = \frac{\int_0^V \exp \left( -\frac{E_a}{RT} \right) dV}{\exp \left( -\frac{E_a}{RT_r} \right)}$$

(2.1)

The calculation of the equivalent reactor volume requires an accurate knowledge of the temperature profile along the tube and of the activation energy, $E_a$. As the
activation energy is not known beforehand, a trial and error procedure must be employed. If available, a good estimate of the activation energy is used as a first guess. This value, coupled with the measured temperature profile, are used to obtain the equivalent reactor volume. The rate constant is then determined. This procedure is carried out at several temperature levels, and using the Arrhenius equation, a new value for the activation energy is obtained. Successive iterations are carried out until the activation energies converge.

A similar procedure may be followed to calculate the equivalent reaction time in a batch reactor. The equivalent reaction time, $t_r'$, is the time required at reference temperature, $T_r$, to produce the same conversion as that obtained in time, $t$, by the actual non-isothermal operation. Written for a first order reaction, the equivalent reaction time is mathematically given as:

$$t_r' = \exp \left( \frac{-E_a}{RT} \right) \int_0^t \exp \left( \frac{-E_a}{RT} \right) \, dt$$

Strictly speaking, the equivalent reactor volume / reaction time concept is only valid for: (1) small temperature differences; and (2) a single reaction with a single activation energy or, alternatively, a set of parallel reactions having identical values of activation energy. If applied to situations in which several reactions occur simultaneously with different activation energies, such as pyrolysis, the results may be erroneous. Despite this fact, many researchers have still applied the concept. Surprisingly, though, this has not led to serious errors. In fact, it has been demonstrated (Van Damme et al., 1975) that, provided the temperature profile of
the reacting gas is well-defined and a reasonably accurate estimate of the activation energy is available, the equivalent reactor volume concept can be confidently applied to pyrolysis studies. They compared the reaction order, frequency factors and activation energies predicted for propane pyrolysis by both the equivalent reactor volume concept and a computationally more demanding straight non-isothermal approach and found complete agreement. Similar observations were observed for naphtha pyrolysis (Van Damme et al., 1981). Regardless, it is still far better to obtain data at near-isothermal conditions.

2.3 CURIE POINT PYROLYSIS

The preceding discussion has highlighted the fact that conventional laboratory reaction systems cannot provide rapid heating of the entire feedstock to an accurately defined temperature with equally rapid quenching after a precisely controlled pyrolysis time. Thus, these systems do not satisfy the criteria for attainment of valid kinetic data nor do they fulfill the conditions necessary for Ultrapyrolysis. Consequently, it is obvious that a new reactor type with a radically different heating concept is required.

Curie point pyrolysis may well provide the closest approach to the ideal pyrolysis system. This technique, introduced by Simon and Giacobbo (1965), employs a novel heating process which ensures rapid temperature rise (within milliseconds) of the feedstock to a precisely known and controlled temperature. Rapid quenching of the pyrolysis products by direct gas mixing follows. In fact, the temperature–time profile attained approximates a half square wave. Thus, the system is generally termed a "pulse-mode pyrolyser". The Curie point pyrolyser
was initially designed as an analytical device for characterization of complex nonvolatile substances, such as polymers, complex biomaterials (blood cells through to spruce needles) and even bitumens (Poxon and Wright, 1971). This device has only recently been discovered as a research tool ideal for the kinetic study of pyrolysis reactions. Egsgaard and Carlsen (1983, 1986) have reported kinetic results for the pyrolyses of several compounds, excepting hydrocarbons. Rastogi (1987) utilized a Curie point pyrolyser to pyrolyse propane. He indicated that this system achieved far better reaction control than that possible with conventional laboratory reactors.

2.3.1 Pyrolyser Operation

In Curie point pyrolysis, a thin ferromagnetic wire, coated with a microgram quantity of sample, is placed inside a low volume glass tube which, in turn, is inserted into a high frequency induction coil. The ferromagnetic wire is composed of a magnetic nickel–iron–cobalt alloy. When the high frequency field is energized, almost instantaneous heating of the ferromagnetic wire, and hence the sample, results. At a temperature which depends only on the alloy composition, termed the Curie point temperature, a transition from ferromagnetism to paramagnetism occurs. At this time, the high frequency energy intake by the wire drops dramatically. Consequently, the wire temperature stabilizes at the Curie point. This temperature is then maintained until the high frequency energy is automatically switched off at the end of a pre-set reaction duration. Hence, pyrolysis under precisely controlled and predetermined temperature and time is achieved. Reproducibility is also ensured since the heating characteristics of the wire depend only on its alloy composition and geometry. Should, however, a different pyrolysis temperature be
desired, all one needs to do is select a different ferromagnetic alloy with the desired Curie point temperature. Wires are available which will stabilize at a number of temperatures ranging from 300 to 1000°C. These extensive features are what makes Curie point pyrolysis so unique and desirable.

Normally, the pyrolysis unit is interfaced to the inlet of a gas chromatograph such that a helium stream flows through the glass tube and past the wire resulting in an effective quench and immediate transfer of the pyrolysis products. As the products are conveyed directly into the gas chromatograph for analysis, losses due to sampling, a common problem with conventional reaction systems, are eliminated.

2.3.2 Theoretical Basis and Implications

High frequency induction heating of ferromagnetic wires is influenced by a number of factors. A clear understanding of the theory behind the pyrolyser operation must be acquired in order to ensure optimal results.

When a high frequency current flows through a coil, it induces, in the interior of the coil, a magnetic field which, in turn, generates a potential in the conductive ferromagnetic wire. Due to the ohmic resistance of the wire, the current thereby induced generates heat. At high frequencies, the induced current is not uniformly distributed across the cross-section of the wire. Rather, it is concentrated at the surface of the wire and penetrates only a short distance (less than 10% of the wire radius) within the wire. This distance is termed the skin depth.
Significant power is consumed by the ferromagnetic wire during heating. Due to the sharp skin effect, the power consumption will depend largely on the rate of power uptake at the surface. This power uptake, which is a good measure of the heating rate, is dependent on a number of variables, as shown in equation (2.3):

\[
N = 2\pi \sqrt{2} H^2 \rho (1/s) F(r,s)
\]  

(2.3)

where,

\[
s = \sqrt{\frac{\rho/\pi\gamma\mu_o\mu_r}{r}}
\]  

(2.4)

* N: power consumption per unit surface  
* H: magnetic field strength inside the coil  
* r: ferromagnetic wire radius  
* \( \rho \): specific electric resistance of the wire  
* s: skin depth of the induced current  
* F: Bessel function depending upon \( r \) and \( s \)  
* \( \gamma \): oscillator frequency  
* \( \mu_r \): relative magnetic permeability  
* \( \mu_o \): permeability of free space

The relative magnetic permeability is a function of material, temperature and magnetic field strength. Ferromagnetic conductors have a permeability ordinarily much greater than one, whereas that of paramagnetic conductors is approximately one. As ferromagnetic materials have such a high relative permeability, they absorb energy very readily when inserted into a high frequency induction coil; thus rapid heating ensues. When ferromagnetic conductors have been heated to a sufficiently high temperature, the normally high relative permeability will drop suddenly to one signaling the onset of paramagnetic behavior.
and thus the Curie point. At this time, an increase in the skin depth occurs, such that it encompasses, in most cases, the entire wire cross-section. Consequently, \(1/s\) and \(F(r,s)\) become smaller and the power consumption of the ferromagnetic wire is drastically reduced. Provided that the wire diameter, oscillator frequency and magnetic field strength are properly matched, such that the energy uptake by the wire is less than or equal to its conductive and radiative heat losses, the temperature of the wire will remain at the Curie point.

In general, the optimal wire diameter for a fast warm-up and a constant end temperature decreases with increasing frequency and has to be defined for each and every oscillator used. For oscillators of about 500 kHz, Bühler and Simon (1970) found that a wire diameter of approximately 0.5 mm was ideal. The corresponding magnetic field strength, which depends on both the oscillator output and induction coil geometry, was 1170 oersted. Under these conditions, an iron wire was heated to its Curie point (770°C) in under 30 ms. This heat-up time is often referred to as the temperature-rise-time (TRT).

Many commercial pyrolysers claim to operate under the same conditions used by Bühler and Simon. However, Levy, Fanter and Wolf (1972) indicated that these units do not quite meet the optimal specifications of Bühler and Simon. Consequently, the commercial units may exhibit longer temperature-rise-times.

If the diameter, frequency and field strength of the pyrolyser are not properly coordinated, unexpected results may be obtained. When Bühler and Simon coupled a 0.1 mm diameter iron wire with a 1 MHz oscillator, they discovered that the wire heated very slowly due to a relatively flat power consumption versus temperature
However, when the frequency was increased to 5 MHz, the power consumption quickly reached a high value and then dropped off, indicating that rapid heating had occurred. Placement of a large diameter wire (2 mm) in the 1 MHz oscillator yielded very different results. Although rapid heating occurred, the power consumption leveled at a value far above zero. Thus, heating of the wire continued and the end temperature far exceeded the desired Curie point. When, however, the oscillator frequency was decreased to 100 kHz, good temperature control was achieved. Upon the recommendation of Oertli (1974), many commercial pyrolysers have implemented two stage power, thus minimizing the overshoot problem. Once the large drop in power uptake is sensed, the power input drops dramatically, thus ensuring that excessive temperatures are not reached.

As mentioned previously, different Curie points are obtained by employing ferromagnetic wires of varying alloy composition. However, variations in the nickel, cobalt and iron content affect not only the Curie point but the temperature-rise-time as well. Correlations between the alloy composition and the corresponding temperature-rise-times (TRT's) indicate that alloys of higher nickel content show increased TRT's while higher cobalt content produces faster TRT's (Levy, Fanter and Wolf, 1972).

2.3.3 Other Considerations

The previous discussion has indicated that, providing certain measures are taken, a Curie point pyrolyser can rapidly heat a ferromagnetic wire, in a reproducible manner, to its Curie point and then maintain this temperature. However, when a sample is applied to the wire with the intent of pyrolysing, other
factors must be considered to ensure that a successful experiment results.

A typical pyrolysis involves: preparation of the sample; the actual pyrolysis of the sample; quenching and transfer of the pyrolysis products away from the pyrolysis zone; and analysis of the products by an instrument, usually a gas chromatograph. In many cases, the first three steps have been the cause of poor results. In particular, poor technique associated with preparation of the sample has been a major problem (Wampler and Levy, 1987).

In order to minimize the thermal and mass transfer gradients, small quantities of sample must be employed. The smaller the sample, the more likely that it will all experience the same temperature at the same time. Hence, the kinetic data obtained from the experiment will be highly accurate. For most commercially available pyrolysers, a sample size in the low microgram range \((5 - 50 \mu g)\) is suggested (Wampler and Levy, 1987). Related to, and as important as, the size of the sample is the manner in which it is applied to the ferromagnetic wire. The most consistent application is afforded by depositing the sample onto the wire in a thin film.

Perhaps the most frustrating problem in Curie point pyrolysis is sample contamination. As the samples must be extremely small to ensure isothermicity, the possibility of contamination is especially great. This is a particular problem if the pyrolysis products are very complex as then it is difficult to determine which peaks result from pyrolysis and which are merely contaminants. Consequently, care must be taken to ensure that all tools used to manipulate the sample material are clean. Under no circumstances, should fingers touch the sample nor those items in
contact with it. As well, the ferromagnetic wires should be cleaned prior to use and disposed after the pyrolysis. The glass tube through which the pyrolysis products pass on their way to the gas chromatograph should also be cleaned before each use.

As the sample is pyrolysed when near or in contact with a hot ferromagnetic wire containing nickel, iron and cobalt, catalytic effects may be of concern. However, except for the pyrolysis of oxygen-containing samples (Egsgaard and Carlsen, 1986), no catalytic activity has been demonstrated (Jackson and Walker, 1971). In fact, the product distributions were not altered by coating them with an inert surface such as gold (Jones and Moyles, 1961). Hence, it is not likely that the hot metal surface will have any effect on hydrocarbon pyrolysis. Nonetheless, further experimental proof is deemed necessary.

Once the sample has been pyrolysed, the resulting products must be quenched and transferred from the pyrolysis zone to the gas chromatograph. As previously noted, a flow of helium accomplishes this. The flow rate of this stream should be maximized in order to ensure both rapid quenching of the products and delivery to the gas chromatograph in a sharp plug. In order to ensure that no condensation and subsequent loss of the products occurs along the way, the glass tube is frequently heated to a temperature equivalent to that employed in the gas chromatograph injection block.

Despite the number of factors that must be considered to ensure a successful Curie point pyrolysis run, there is no doubt that this is still, by far, the best reaction system available for determination of pyrolysis kinetics.
2.4 HEAVY HYDROCARBON PYROLYSIS RESEARCH

Although hydrocarbon pyrolysis has been a subject of intense research over the past 100 years, heavier compounds (C$_5^+$) have largely been excluded from study. Rather, most studies have been restricted to light paraffins such as ethane, propane, and butane. This is primarily due to the fact that pyrolysis is a non-selective process. Thus, as heavier and heavier reactants are pyrolysed, the complexity of the product mixture increases dramatically. It was not until the widespread application of sophisticated analytical techniques, such as gas chromatography and gas chromatography–mass spectrometry, that it became possible to identify and quantify the vast products of heavy hydrocarbon pyrolysis. Due, in part, to this fact and also to the growing importance of heavier feedstocks to supply the world ethylene demand, a large number of publications have appeared over the past 25 years dealing specifically with heavy hydrocarbon pyrolysis.

Typical heavy hydrocarbon feedstocks, such as naphtha, gas oil and even vacuum gas oil, are composed of hundreds of compounds, ranging from n-paraffins to naphthenes to aromatics. In order to properly understand the pyrolysis of these heavy feedstocks, from a scientific "point of view", one must first understand the pyrolysis of the pure components which make up the complex mixture. Following this, interactions between the major components types should be studied. Only after this stage has been completed, should the whole feedstock be studied. This approach has been followed by many researchers, most notably by G.F. Froment and co-workers (Laboratorium voor Petrochemische Techniek, Rijksuniversiteit, Gent, Belgium).
It is only logical that the literature pertaining to heavy hydrocarbon pyrolysis should be presented in a sequence similar to that in which it has been studied. The pyrolysis of pure heavy paraffins, both normal and branched, will be discussed first, followed by heavy olefins, naphthenes and, finally, aromatics. Although few detailed studies pertaining to pyrolysis of mixtures exist, a brief discussion will be presented. As well, the pyrolysis of naphthas and gas oils will be briefly mentioned. Finally, the effect of diluent gases, trace oxygen and the reactor surface on hydrocarbon pyrolysis will be discussed.

2.4.1 Pyrolysis of Heavy Paraffins

The pyrolysis of pure paraffins, from pentane through tetracosane (C\textsubscript{24}) (Blouri \textit{et al.}, 1981), has been studied by numerous researchers over the past few decades. In particular, n–hexadecane has been the subject of research on numerous occasions (Zhou \textit{et al.}, 1987; Depeyre \textit{et al.}, 1985; Rebick, 1981; Groenendyk \textit{et al.}, 1970; Fabuss \textit{et al.}, 1962; Panchenkov and Baranov, 1958; Voge and Good, 1949). Most of the heavy paraffin studies have been conducted on normal paraffins, and as a result, a clear understanding of n–paraffin pyrolysis now exists. Although the pyrolysis of branched paraffins is rarely studied, it is believed that they behave in a similar manner, with few variations.

2.4.1.1 Product Distributions

It has been demonstrated on numerous occasions that at low conversions (approximately less than 10%) and low pressures (few atmospheres or less), higher paraffins selectively crack to form olefins, methane and ethane as primary products.
(Rebick, 1983). Small amounts of hydrogen and propane are also formed; however, no paraffins higher than propane will appear. Although ethylene and propylene are the most prevalent olefins, the entire range of olefins up to \( n-1 \), where \( n \) denotes the number of carbon atoms in the feedstock paraffin, are produced. Normal paraffins always produce only straight-chain products; thus, the olefins are only 1-olefins. Branched paraffins, on the other hand, do yield some branched products and thus olefins with internal double bonds are produced as primary products (Rebick, 1983).

As the conversion level is increased (either by an increase in the temperature and/or residence time), the product distribution deviates from that present at low conversions; secondary reactions are the cause. Initially, the higher 1-olefins rapidly decompose into lower 1-olefins and then light gases (methane through to butenes). At moderate conversion levels, diolefins, in particular butadiene, begin to appear. As the conversion is pushed still higher, the \( C_4 \)'s and propylene decompose, yielding still more methane and ethylene and, as well, aromatics and heavier products. Meanwhile, at temperatures exceeding 750°C and high conversion, trace production of acetylene is noted (Depeyre et al., 1985).

2.4.1.2 Free–Radical Chain Mechanism

It has frequently been shown that paraffin pyrolysis behaves as an approximately first order reaction in the temperature and pressure range of industrial pyrolysis (Froment, 1981), although inhibition is observed. Typically, the first order rate constant increases with increasing molecular weight. For example, correlation of pyrolysis data obtained at 500°C and 1 atm (Voge and Good, 1949) yielded rate constants of \( 7.14 \times 10^{-5} \text{ s}^{-1} \) for \( n \)-butane and \( 3.18 \times 10^{-3} \text{ s}^{-1} \) for
n-hexadecane.

Reported activation energies for pyrolysis of normal paraffins heavier than hexane are 60 ± 5 kcal/mol (Fabuss et al., 1964). Generally a slight decrease in the activation energy accompanies an increase in carbon number. Branched paraffins possess a slightly lower activation energy as they crack more readily.

It is well known that the pyrolysis of hydrocarbons, like most thermal homogeneous gas-phase reactions, proceeds by a free-radical chain mechanism, as first proposed by Rice (1931). The Rice–Herzfeld (or Simple Rice) model (Rice and Herzfeld, 1934) is able to explain the approximately first order kinetic relationship and also why the observed activation energy (55 – 65 kcal/mol) is substantially less than that required to break a carbon–carbon bond. One aspect of the free-radical theory developed by Rice and collaborators is an explanation for the distribution of products found in hydrocarbon pyrolysis. In fact, this model has successfully predicted the product distributions of light alkane (methane to n-butane) pyrolysis, especially at low conversions and low pressures.

In 1943, Rice and Kossiakoff (Kossiakoff and Rice, 1943) noted that the Rice–Herzfeld model, particularly in the case of higher hydrocarbons (n-hexane and heavier), over-predicted the ethylene yield and under-predicted the higher liquid olefin yields. Thus, isomerization of higher alkyl radicals was added to the model and the modified Rice–Kossiakoff model came into being.

The Rice–Kossiakoff generalized free-radical chain mechanism predicts that radical reactions involved in pyrolysis can be classified into three broad categories:
initiation; propagation, consisting of hydrogen abstraction, radical decomposition and radical isomerization; and termination.

1. Initiation Reactions:

Free radicals are introduced into the reaction system through thermal splitting of the n-paraffin at its weakest bond. As single carbon–carbon bonds are normally weaker than carbon–hydrogen bonds, it is necessary to consider only the former.

\[ C_nH_{2n+2} \rightarrow R_i^\cdot + R_j^\cdot, \quad i + j = n \]  

(2.5)

\( R_i^\cdot \) and \( R_j^\cdot \) denote primary radicals. Only a small fraction of the feedstock is involved in initiation, so that the influence of this type of reaction on the product distribution is usually negligible (Froment, 1981). However, as noted above, the activation energy for initiation is significantly greater than that for the overall decomposition (75 – 80 versus 55–65 kcal/mol), and, hence, the initiation step has a major effect on the global rate of reaction and can affect the product distribution likewise. As temperature is increased, the ratio of the total reaction rate to the rate of initiation (termed, the chain length) decreases, thus forcing the initiation and termination products to make up a larger fraction of the total.

2. Propagation Reactions:

This category encompasses a series of reactions that convert reactants to products while essentially leaving the radical concentrations unchanged. The first step of propagation is the transfer of hydrogen from an n-paraffin molecule to a small primary radical. A stable molecule is formed along with a large alkyl radical:

\[ R_\beta^\cdot + C_nH_{2n+2} \rightarrow R_\beta^\cdot H + C_nH_{2n+1}^\cdot \]  

(2.6)

In the second step, the large alkyl radical decomposes rapidly and
unimolecularly into a 1-olefin and another radical, $R_k$:

$$C_nH_{2n+1}^\cdot \rightarrow 1\text{-olefin} + R_k^\cdot$$  \hspace{1cm} (2.7)

This new radical, in turn, decomposes until a second generation $R_\beta^\cdot$ radical, the chain carrier, is formed. The chain carriers are usually methyl and ethyl radicals. Radical decomposition is normally governed by the "$\beta$-bond breaking" rule. This rule states that the bond which breaks is one bond over from the bond to which the radical carbon atom is attached. Decomposition of the large alkyl radical is assumed to be faster than a bimolecular reaction with another hydrocarbon. Hence, chain carriers are readily formed and go on to abstract hydrogen from another $n$-paraffin molecule, thus continuing the chain reaction.

The absence of paraffins heavier than propane in $n$-paraffin pyrolysis suggests that at low pressures, the hydrogen transfer reaction is slow relative to radical decomposition.

Kossiakoff and Rice accounted for ethylene over-prediction, in the case of higher $n$-paraffin pyrolysis, by proposing that, prior to radical decomposition, the large alkyl radicals isomerize by coiling back on themselves and then internally transferring hydrogen between carbons five atoms apart on the chain:

$$C_mH_{2m+1}^\cdot \rightarrow C_mH_{2m+1}^\cdot, \quad (m \geq 6)$$  \hspace{1cm} (2.8)

This is a reaction involving a six-membered ring transition state. More recently, Rumyantsev et al. (1975) suggested that primary radicals can isomerize through 1-4, 1-5, 1-6 and 1-7 intramolecular hydrogen transfers, thus progressing through 5-, 6-, 7- and 8-membered rings, respectively.

3. Termination Reactions:

At this stage, the radicals either combine directly to yield an alkane
or alkene, or split unevenly (disproportionate) to form stable products:

$$R_0^\cdot + R_p^\cdot \rightarrow \text{products}$$  \hspace{1cm} (2.9)

Generally, the influence of the termination stage on the product distribution is negligible, except at elevated temperatures, as noted above. However, the reaction order is established at this time. The combination of a large alkyl radical and a radical formed through radical decomposition yields an order of unity.

Over 50 years after it was proposed, the Rice–Kossiakoff reaction mechanism is still considered to be the best explanation for the product distributions of higher paraffin pyrolysis. However, the mechanism is limited, in that it provides a good prediction of the product distributions only at low pressures and fairly low conversions. The model is not capable of predicting the secondary reaction schemes that drastically alter the product distribution as conversion is increased. As well, it is not capable of foreseeing the production of molecular hydrogen. More importantly, though, is the fact that very few low conversion studies have been performed at temperatures much above 650°C. Hence, it is unclear whether the Rice–Kossiakoff mechanism will hold at temperatures of commercial interest.

2.4.1.3 Secondary Reaction Mechanisms

An increase in conversion results in two changes: (1) the product distribution is altered; and (2) the rate constant for paraffin disappearance is reduced. The latter is due to product inhibition and will be discussed later. The former, however, is caused by secondary reactions, as noted previously. When increasing the temperature and/or reaction time, the decomposition of higher olefins
is first noted. As the rates of decomposition of these olefins are comparable to that of the feedstock paraffin, they rapidly decompose to lighter olefins as the conversion is increased. These light olefins, in turn, decompose to ethylene, methane and hydrogen. A detailed description of the different mechanisms of olefin decomposition will be given in Section 2.4.2.

Butadiene, which is observed at moderate conversions (greater than 40%), is thought to result from hydrogen abstraction, followed by \( \beta \)-scission, of 1-butene (Billaud and Freund, 1986), as follows:

\[
1-C_4H_8 + R \cdot \rightarrow 1-C_4H_7\cdot + RH \tag{2.10}
\]

\[
1-C_4H_7\cdot \rightarrow 1,3-C_4H_6 + H\cdot \tag{2.11}
\]

Similarly, the production of acetylene at high conversions (greater than 90%) can be explained by the reaction (Depeyre et al., 1985):

\[
H \cdot + C_2H_4 \rightarrow H_2 + C_2H_3\cdot \tag{2.12}
\]

\[
C_2H_3\cdot \rightarrow C_2H_2 + H\cdot \tag{2.13}
\]

The secondary formation of aromatics, such as benzene, toluene, styrene and naphthalene, which first appears at moderate conversions, can be interpreted by a Diels–Alder mechanism involving ethylene or propylene and 1,3-butadiene (Billaud and Freund, 1986) and cyclic olefins as intermediates:

\[
\begin{align*}
C\cdot\text{CH}_2 + \text{CH}_2 & \rightarrow \text{C}_6\text{H}_6 \\
\text{C}\cdot\text{CH}_2 + \text{CH}_2 & \rightarrow \text{C}_6\text{H}_6 + 2\text{H}_2
\end{align*}
\tag{2.14}
\]

\[
\begin{align*}
\text{HC} = \text{CH}_2 + \text{H}_2\text{C} = \text{CH}_3 & \rightarrow \text{C}_6\text{H}_5\text{CH}_3 \\
\text{HC} = \text{CH}_2 + \text{H}_2\text{C} = \text{CH}_3 & \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + 2\text{H}_2
\end{align*}
\tag{2.15}
\]
Benzene can also be formed by the bimolecular reaction of two propenyl radicals, as follows (Billaud and Freund, 1986):

\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH} \cdot \text{CH}_2 \\
\text{H}_2\text{C} &= \cdot \text{CH} = \text{CH}_2 \\
\rightarrow & \text{Cyclic structure} \\
\rightarrow & \text{Benzene} + 2\text{H}_2
\end{align*}
\]

(2.16)

Finally, benzene can be produced by direct cyclization of 1-hexene (Billaud and Freund, 1986):

\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH}_2 \cdot \text{CH}_2 \\
\text{H}_2\text{C} &= \cdot \text{CH} = \text{CH}_2 \\
\rightarrow & \text{Cyclic structure} \\
\rightarrow & \text{Benzene} + 3\text{H}_2
\end{align*}
\]

(2.17)

It is now obvious that polycyclic hydrocarbons can be formed by a series of Diels–Alder reactions involving olefins, or aromatic hydrocarbons, and butadiene. Thus, naphthalene (two-ring polyaromatic) might be formed by addition of butadiene to benzene; and, similarly, phenanthrene and anthracene (three-ring polyaromatics) might be formed from butadiene and naphthalene and so on. In the end, very complex, high molecular weight multi-ring polyaromatics, highly deficient in hydrogen, are formed. They constitute a fraction commonly referred to as coke.

\[2.4.1.4 \text{ Inhibition}\]

Inhibition is often discussed within the pyrolysis literature and refers to a decrease in the global first order rate constant with increasing conversion. This phenomenon reflects variations in the free–radical mechanism at high conversions (greater than 90%), which are likely caused by olefins, known to be good inhibitors of free–radical reactions. It is probable that the \(R_\beta\) radical reacts with propylene and \(C_4\)– olefins, yielding less active stabilized alkyl radicals, so that the chain
mechanism is slowed down.

2.4.1.5 Effect of Pressure

Pressure affects both the rate and the product slate of paraffin pyrolysis. As pressure is raised, the first order rate constant actually increases very gradually, thus causing an increase in conversion. Typically, the rate constant doubles when the pressure is raised from 1 to 50–100 atm (Fabuss et al., 1964).

Very dramatic changes occur in a pyrolysis product stream when the pressure is significantly increased. This increase causes the hydrogen abstraction rate to exceed that of radical decomposition. As a result, the large alkyl radicals are stabilized by hydrogen abstraction before they can decompose into short β−radicals. Thus, paraffins ranging from methane to n−pentadecane are formed. At the highest pressures (about 150 atm), equal amounts of paraffins and olefins are formed (Doue and Guiochon, 1968), indicating that the n−paraffin radical only decomposed once before being stabilized by hydrogen transfer.

Another interesting aspect of elevated pressure (greater than 50 atm) pyrolysis is the formation of hydrocarbons heavier than the feed component at relatively low conversions. These products are presumably formed from alkylation reactions in which the large alkyl radical added to an olefin to form a large paraffin.

In general, the effects discussed above only occur when the pressure is significantly greater than atmospheric. When the pressure is no higher than, say, 3 atm, all that can be expected is a slight increase in the ethane and propane
production and, at high conversions, a possible increase in the aromatics yield as well (Babash et al., 1974).

2.4.2 Pyrolysis of Heavy Olefins

The pyrolysis of heavy olefins is of interest because such compounds are among the primary products of heavy paraffin pyrolysis. The decomposition of these olefins is a significant secondary reaction process at high conversions typical of commercial operation. Heavy olefins decompose by free—radical reaction paths similar to paraffins, in that the propagation stage consists of both hydrogen transfer and radical decomposition steps. However, no generalized mechanism like that of Rice's for paraffin pyrolysis has been proposed. The primary products of olefin and paraffin pyrolysis are similar. For conversions of less than ten percent, the entire range of 1—olefins lighter than the reactant as well as hydrogen, methane and ethane are produced. Once again, ethylene and propylene dominate the olefins. However, significant differences do exist between olefin and paraffin pyrolysis. An entire range of diolefins lighter than the reacting olefin, as well as small yields of cyclic olefins, are observed as primary products. As well, larger than expected yields of propylene and the \( \text{C}_n-3\text{H}_{2n-6} \) olefin are noted (Rebick, 1983).

Olefins exhibit kinetic trends which are similar to those noted for paraffins. In both cases, the cracking rate increases slowly with increasing molecular weight. However, the global reaction order for olefin pyrolysis tends to be somewhat greater than unity (eg. dodecene pyrolysis — order = 1.33; Rebick, 1979). Activation energies for olefins are typically 5—10 kcal/mol lower than that of the corresponding paraffin (Rumyantsev et al., 1975). As well, the rates of decomposition are slightly
higher (Rebick, 1979), indicating that olefin pyrolysis proceeds more readily than for paraffins.

Different mechanisms have been suggested for the decomposition of 1-olefins. However, the product distribution is best rationalized by assuming that the decomposition occurs by three parallel reaction pathways — one molecular and the other two free–radical (Rumyantsev et al., 1975). Miller (1963) proposed the molecular mechanism, entitled the "retro–ene reaction", which produces propylene and a 1-olefin via a ring transition state:

\[ C_nH_{2n} \rightarrow C_3H_6 + C_{n-3}H_{2n-6} \]  

(2.18)

This pathway accounts for the two large peaks in the olefin product distribution. The remaining products can be accounted for by two free–radical pathways. Radicals are formed during the initiation stage both by carbon–carbon and carbon–hydrogen bond fission. In the first pathway (Miller, 1963), a large (parent) radical is created by hydrogen abstraction from the reactant by small radicals (R·). These chain carriers are likely CH₃· and C₂H₅·, and to a lesser extent, H· and C₃H₅·.

\[ C_nH_{2n} + R^• \rightarrow RH + C_{n-1}H_{2n-2} \cdot \]  

(2.19)

The parent radicals formed then decompose through β-scission, as in paraffin pyrolysis, to form both 1–olefins, diolefins and cyclic olefins, as well as new radicals. These radicals, in turn, decompose until small and then undergo hydrogen abstraction, thus continuing the chain. It should be noted, that provided the chain is sufficiently long, intramolecular isomerization of the olefinic radical prior to hydrogen abstraction can occur, as in paraffin pyrolysis.

This mechanism accounts for all the products except the \( C_{n-1}H_{2n-2} \) and
$C_{n-2}H_{2n-4}$ olefins. These olefins are likely derived from heavier parent radicals, which themselves are formed by the addition of chain carriers (small radicals) to the reactant olefins, followed by decomposition through $\beta$-scission (Rebick, 1979). Typical addition reactions are as follows:

$$C_nH_{2n} + \begin{cases} \text{H}^* \\ \text{CH}_3^* \\ \text{C}_2\text{H}_5^* \end{cases} \rightarrow \begin{cases} C_{n+1}H_{2n+3}^* \\ C_{n+2}H_{2n+5}^* \\ C_{n+2}H_{2n+5}^* \end{cases}$$ (2.20)

The overall mechanism, then, is the sum of the contributions of three paths (Rebick, 1979):

1. Molecular decomposition into $C_3H_6$ and $C_{n-3}H_{2n-6}$;
2. Free-radical chain mechanism with parent radical $C_nH_{2n-1}$;
3. Free-radical chain mechanism with parent radicals $C_nH_{2n+1}$, $C_{n+1}H_{2n+3}$ and $C_{n+2}H_{2n+5}$.

This reaction mechanism qualitatively accounts for all of the observed products and, as well, supports the measured reaction orders. Path 1 is certainly first order in reactant. Paths 2 and 3 may be one-half, first or three-halves order, depending on the termination reaction. Most likely, the termination stage involves combination or disproportionation of the chain-carrying radicals (three-halves order). Thus, with a first order initiation stage, this would result in three-halves order kinetics. The overall reaction order would then be somewhere between first (Path 1) and three-halves (Paths 2 and 3); this agrees with experimental results.

Unfortunately, the product distribution obtained from olefin pyrolyses cannot be predicted with any quantitative certainty, unless some additional assumptions of radical stabilities are incorporated into the above mechanism.
(Rebick, 1983). As well, this mechanism is not capable of describing the pyrolysis of internal olefins without substantial modifications (Giraud—Horvilleur and Blouri, 1977).

2.4.3 Pyrolysis of Naphthenes

Pyrolysis feedstocks, although mostly composed of paraffins, also contain naphthenes and other hydrocarbons. In virgin (never reacted) feedstocks, the naphthenes are alkylated. Unfortunately, the pyrolysis of pure alkylated naphthenes has not been reported. However, there are published studies for unsubstituted naphthenes, in particular cyclohexane (Virk et al., 1979; Levush et al., 1969), decalin and tetralin (Virk et al., 1979). These three compounds simulate unsubstituted naphthenes in the naphtha, kerosene and atmospheric gas oil boiling ranges, respectively. In general, naphthenes are slightly more refractory than paraffins, as reflected in the slightly higher activation energy (approximately 64 kcal/mol; Szepesy et al., 1977). As a result, it is likely that side chain cracking would dominate the pyrolysis of alkylated naphthenes. Nevertheless, a brief description of the reaction mechanism of pure naphthenes is in order.

Higher temperatures have been employed (800 – 900°C) to pyrolyse unsubstituted naphthenes, due to their higher activation energy (Virk et al., 1979). The product distributions obtained for these pyrolysies have best been rationalized by assuming that decomposition occurs through a radical mechanism. For example, it is well established that cyclohexane pyrolysis is initiated by carbon—hydrogen bond scission. This initial reaction is slow, thus accounting for the more refractory nature of naphthenes. The initiation stage is followed by β-scission and ring
opening of the cyclohexyl radical. The resulting hex-1-ene-6-yl radical decomposes to finally yield ethylene, 1,3-butadiene and a hydrogen atom, the chain carrier (Virk et al., 1979).

Despite the fact that they do not contain alkyl side chains, decalin and tetralin, which possess branched carbon atoms, are good analogs of the naphthenic fraction present in commercial feedstocks. The pyrolysis of decalin is quite complex, owing to the fact that three types of decalyl radicals are possible and each is open to a variety of decomposition routes. Following initiation, the lengthy decalyl radical is subjected to the classical Rice–Kossiakoff isomerization; this also has the effect of expanding the product spectrum. Nevertheless, the mechanism proceeds as for cyclohexane and the decalyl radical decomposes to eventually form ethylene, butadiene and benzene, the dominant products, as well as a hydrogen atom (Virk et al., 1979). The primary products of tetralin pyrolysis (ethylene, butadiene, hexatriene and benzene) are accounted for by a similar mechanism.

The fact that naphthenes can readily dehydrogenate has not yet been discussed. This process could quite likely supersede the radical mechanism described above so as to produce aromatics, polyaromatics and, in the end, coke.

2.4.4 Pyrolysis of Aromatics

Aromatics are also present in virgin pyrolysis feedstocks, and like naphthenes, they are most often alkylated. Unsubstituted aromatics are also of interest as they are products of high conversion hydrocarbon pyrolysis. The literature on aromatics pyrolysis is fairly prevalent, particularly for unsubstituted
compounds. Thus, a detailed discussion of unsubstituted aromatic pyrolysis is warranted. A brief mention of the work to date concerning alkylated aromatic pyrolysis will follow.

2.4.4.1 Unsubstituted Aromatics

Unsubstituted aromatic hydrocarbons are remarkably resistant to pyrolysis. Benzene, the simplest of aromatic compounds, is the most refractory hydrocarbon. It is unlikely, at commercial temperatures of 600 - 850°C, that it would undergo any substantial amount of decomposition through ring fission (Badger, 1965); carbon–carbon double bonds require an immense amount of energy to break. However, carbon–carbon single bonds and carbon–hydrogen bonds are readily ruptured at these temperatures to give radicals. Thus, the primary process in the pyrolysis of benzene is the fission of a carbon–hydrogen bond to give phenyl radicals. These radicals then react with further benzene molecules to give biphenyl, as shown in reaction (2.21). Further phenylation of biphenyl would give terphenyl, and cyclodehydrogenation of terphenyl would yield triphenylene, as shown, and so on. In such a manner, a variety of condensed polyaromatic hydrocarbons are formed.

The pyrolysis of more complex aromatic hydrocarbons, such as naphthalene, phenanthrene and anthracene, proceeds in much the same manner. Thus, a
generalized mechanism for unsubstituted aromatic pyrolysis can be postulated. Carbon—hydrogen bonds are ruptured at higher temperatures to give aryl radicals which then react further to give biaryls, which undergo cyclodehydrogenation to form condensed polyaromatics. Another reaction path is available, though. Recent work on the pyrolysis of complex polyaromatics has shown that hydrogenation of aromatic rings can occur at high temperatures (greater than 700°C) (Badger, 1965). The hydrogen originates from the fission of the carbon—hydrogen bonds, as described above. For example, hydrogenation of naphthalene yields tetralin, a product often encountered in pyrolysis tars.

2.4.4.2 Alkylated Aromatics

The pyrolysis of alkylated aromatics is far more complex than for unsubstituted aromatics, due to the presence of the side chain. There are several different types of carbon—hydrogen bonds available. Carbon—carbon single bonds are also prevalent. Due to the likeliness that these would undergo rapid fission, it is presumable that side chain cracking will dominate the pyrolysis of alkylated aromatics. Several publications have reported the pyrolysis of alkylated aromatics, such as toluene, ethylbenzene, n—propylbenzene and n—butylbenzene (Badger, 1965) and, more recently, dodecylbenzene (Blouri et al., 1981).

The pyrolysis of toluene was first studied by Berthelot in 1866, and it has been further investigated by many subsequent workers. It has been well established that fission of the \( \text{C}_6\text{H}_5—\text{CH}_3 \) bond occurs to form benzyl and hydrogen radicals, followed by hydrogen abstraction, to yield benzene as a major product. The pyrolysis process is slightly modified for the case of aromatics with longer side
chains (ethylbenzene, n-propylbenzene, etc.). In these hydrocarbons, the saturated carbon–carbon bonds are the weakest and thus break rather readily at high temperatures to initiate the free–radical reaction mechanism. Thus, in the case of n-propylbenzene, phenyl and propyl; benzyl and ethyl; and phenethyl and methyl radicals would be the primary fission products (Badger, 1965):

\[
C_9H_{12} \rightarrow \begin{cases} 
C_6H_5^- + C_3H_7^- \\
C_7H_7^- + C_2H_5^- \\
C_8H_9^- + CH_3^- 
\end{cases} \quad (2.22)
\]

The alkyl radicals would then lose hydrogen to give propylene and ethylene. The aromatic radicals, on the other hand, would abstract hydrogen from n-propylbenzene and the resulting propylbenzene radical would decompose further (Badger, 1965), until another chain carrier (CH$_3^-$) was formed.

\[
C_9H_{12} + \begin{cases} 
C_6H_5^- \\
C_7H_7^- \\
C_8H_9^- 
\end{cases} \rightarrow C_9H_{11}^- + \begin{cases} 
C_6H_6^- \\
C_7H_8^- \\
C_8H_{10}^- 
\end{cases} \quad (2.23)
\]

\[\rightarrow C_8H_8^- + CH_3^- \]

In such a way, benzene, toluene, naphthalene and large quantities of styrene are produced.

All alkylated benzenes will follow a reaction path along the same lines as that outlined above for n-propylbenzene. Interestingly enough, gaseous products are not the major constituents; rather, aromatic liquids dominate the product distribution. The production of simple aromatics (benzene, toluene and styrene) is, as well, always accompanied by polyaromatics, such as naphthalene. The number of polyaromatics formed will increase dramatically as the side chain length is increased. A study on the pyrolysis of n-butylbenzene found that the optimum
temperature for the formation of these polyaromatic hydrocarbons is surprisingly low, at only 700°C (Badger et al., 1964). Thus, the formation of tars and cokes, through further polymerization of the aromatic rings, is a real threat.

2.4.5 Pyrolysis of Hydrocarbon Mixtures

The pyrolysis of pure hydrocarbons has been discussed in detail. However, in order to translate this information into an understanding of the pyrolysis of real feedstocks, such as naphthas, gas oils and whole crudes, one must understand how the various hydrocarbon groups interact with each other when pyrolysed in admixture. It is known that a simple additivity rule is not adequate for the prediction of the product distribution of mixture pyrolysis, as interactions do have a significant effect (Froment et al., 1977). This is likely due to the fact that hydrocarbon pyrolysis is a free–radical mechanism. Therefore, the radical intermediates produced by one component may interact with those produced by another, or the other reactant itself. Consequently, the reaction mechanism would be altered, thus yielding a modified end product distribution.

Mixture interactions can be readily studied by employing simple binary mixtures of pure hydrocarbons. Despite this fact, few such studies have been conducted on mixtures of heavy (C₅⁺) hydrocarbons. However, much work has been carried out on light hydrocarbon mixtures, and the observations should be transferable to heavier materials (Rebick, 1983).
2.4.5.1 General Principles

Based on the research carried out on light hydrocarbon mixtures, some general principles have been developed to describe the interactions. They are as follows (Rebick, 1983):

1. Components that pyrolyse by similar mechanisms have little effect on each other. The reason is obvious — no new radical intermediates can be introduced by either component into the mechanism of the other.

2. However, if two components of very different cracking rates are pyrolysed together, the more refractory of the two tends to inhibit the pyrolysis of the more reactive component while the latter accelerates the pyrolysis of the former. In particular, if a component is refractory because of a slow initiation step (e.g. difficulty in breaking a bond), its pyrolysis will be enhanced by the addition of a less refractory material without any significant reverse inhibition. Conversely, if a component is refractory because the radical intermediates it forms during pyrolysis are stable, then it will have a significant inhibiting effect on the pyrolysis of more reactive materials.

Examples of paraffin—paraffin, paraffin—olefin, paraffin—aromatic and, finally, aromatic—aromatic binary mixture pyrolysis will elaborate on these principles.

2.4.5.2 Paraffin — Paraffin Mixtures

In general, the pyrolysis of heavy paraffins, individually or in multi-component mixtures, produces the same major products. This has been the findings of two separate studies, one involving octane–nonane mixtures (Shah et al.,
1973) and the other concerning multi-component mixtures of paraffins ranging from nonane to docosane (Zhou et al., 1987). The product slates of paraffins pyrolysed in admixture seem to be a combination of those formed by the individual paraffins; no new products are produced. As well, the rate constants are slightly, if at all, altered by mixture pyrolysis. Thus, it is apparent that heavy paraffins do not interact when pyrolysed. This can be explained by the fact that the large alkyl radicals rapidly decompose to form common small radicals. Thus, the large radicals are unable to react to form new species. Similar results have been obtained for light paraffin mixtures, with the exception of those mixtures containing ethane. At moderate conversions, the pyrolysis of ethane is significantly accelerated by the presence of a higher paraffin, whereas at higher conversions, the olefins produced by the higher paraffin inhibit the ethane pyrolysis. However, as ethane is not present in typical liquid feedstocks, interactions between paraffins can be neglected.

2.4.5.3 Paraffin—Olefin Mixtures

Generally, olefins inhibit, as discussed in Section 2.4.1.4, the pyrolysis of paraffins. Normally, the conversion of the olefin is unaltered, or even slightly increased, whereas the conversion of the paraffin is dramatically decreased (Rebick, 1983). The most dramatic effects are observed in the cracking of paraffins with propylene. It is believed that the olefins react with the \( R_\beta \) radicals, yielding stabilized alkyl radicals. Regeneration of the chain carriers through hydrogen abstraction and subsequent radical decomposition is thus prevented. Consequently, the chain mechanism is dramatically retarded. As olefins are not present in virgin pyrolysis feedstocks, this phenomenon is only of concern at high conversions (greater than 90%) when olefins (particularly light olefins) are very prevalent and thus able
to inhibit the pyrolysis process.

2.4.5.4 Paraffin — Aromatic Mixtures

Pyrolysis studies of paraffin—aromatic binary mixture pyrolysis are virtually nonexistent in the literature. However, based on the general principles given above, it is likely that the more refractory aromatics would tend to inhibit the pyrolysis of the more reactive paraffins. Meanwhile, given the low pressures and high temperatures of commercial pyrolysis, a large number of paraffin radicals would be available to interact with the refractory aromatics, thus leading to an increased aromatic conversion. The lack of published data, however, has prohibited proof of these hypotheses.

2.4.5.5 Aromatic — Aromatic Mixtures

There is every reason to believe that the pyrolysis of aromatic mixtures is an important route to the formation of many polycyclic aromatic hydrocarbons. Alone, aromatics are very refractory, but when, say, benzene, naphthalene, phenanthrene and/or pyrene are combined at high temperatures, the formation of even more complex aromatics is inevitable. For example, the co—pyrolysis of naphthalene and benzene (Badger, 1965) would be expected to yield fluoranthene through intermediate steps of phenylation and cyclodehydrogenation, as shown below:

\[
\text{C}_6\text{H}_6 + \text{C}_{10}\text{H}_{12} \rightarrow \text{C}_{19}\text{H}_{12}
\]

(2.24)

Given very high severity cracking, fluoranthene could, in turn, undergo further
reaction yielding even more complex high–boiling polyaromatics and, in the end, coke. Phenanthrene (three–ring polyaromatic) and benzene and, finally, pyrene (four–ring polyaromatic) and benzene co–pyrolysis have yielded similar results (Badger, 1965). Thus, it is certain that the co–pyrolysis of aromatics can lead to very undesirable results.

2.4.6 Pyrolysis of Naphthas and Gas Oils

The pyrolysis of pure components and pure component mixtures have been discussed in detail up to this point. However, in order to extrapolate the findings to real feedstocks such as naphtha and gas oil, the characteristics of these feeds must be identified. It should be understood that the characteristics given below are averaged and do not necessarily correspond to every naphtha or gas oil feedstock.

Straight–run naphtha is currently the most significant feedstock for industrial pyrolysis (Nowak and Günschel, 1983). This highly paraffinic feedstock typically has a boiling range of 40 to 170°C and a mean carbon number of between C₆ and C₇. Normal and branched paraffins typically account for 65 - 80 wt% of the components present; the normal paraffins are usually slightly more prevalent. Simple (one ring) naphthenes and aromatics comprise the remainder; the aromatics content rarely exceeds 5 wt% (Van Camp et al., 1985). Consequently, it is expected that naphtha pyrolysis should proceed in a manner similar to paraffin pyrolysis with slight inhibition due to the presence of naphthenes and aromatics. In naphtha pyrolysis studies, the product distribution has indeed proven to be similar to that achieved by pyrolysis of pure n–hexane pyrolysis. Kumar and Kunzru (1985) identified ethylene, propylene, 1–butene, 1–pentene, methane and ethane as
primary products. The production of significant amounts of hydrogen, methane, diolefins and aromatics was also noted at high conversions. An overall activation energy of approximately 53 kcal/mol was established for naphtha pyrolysis over a temperature range of 720 – 800°C (Kumar and Kunzru, 1985).

After the oil crisis of 1973, a number of olefin plants shifted to feedstocks of kerosene, gas oil or even vacuum gas oil. Gas oil is a heavy mixture with a mean carbon number of about C\textsubscript{16} and a boiling range of 200 – 360°C (Van Camp \textit{et al}., 1985). It is, like naphtha, fairly paraffinic (approximately 85 wt%) with aromatics comprising approximately 10 wt% and naphthenes the remainder. The normal paraffins are slightly more prevalent than their isomers. In contrast to naphtha fractions, the aromatics and naphthenes present in gas oils are often polycyclic entities. Due to this fact, the pyrolysis of gas oils yields smaller yields of light olefins and a greater amount of by-products. In particular, a large quantity of pyrolysis oil, a highly aromatic fraction which boils above 200°C, is produced. Coke production is also significant. Green \textit{et al} (1975) confirmed that complex aromatics are indeed responsible for the olefin yield decrease and significant by-product increase. In their study of the pyrolysis of differently structured C\textsubscript{16} hydrocarbons, which represent compounds with a mean molecular weight of a gas oil fraction, they found that the ethylene yield varied from 33 wt% for n-hexadecane to only 4.3 wt% for highly refractory tricyclic aromatic hydrocarbons. These results indicate how strongly pyrolysis depends on the hydrogen content and, hence, the chemical composition of the gas oil fraction.
2.4.7 Effect of Non–Hydrocarbon Gases and Reactor Surface

2.4.7.1 Steam and Inert Gases

In many pyrolysis studies, nitrogen or steam is employed as a diluent in the tubular–flow reactor in order to control hydrocarbon partial pressure. As previously mentioned, steam dilution is also common commercial practice. In either case, these inert gases are thought to have no direct effect on the homogeneous pyrolysis reactions. This belief is supported by theory. Given that pyrolysis reactions are approximately first order, the reaction rate constant should be independent of feed concentration. Thus, dilution with an inert gas should not affect it. Steam, however, may have an indirect effect on the pyrolysis. This stems from reactions occurring between the steam and coke adhered on reactor surfaces. This topic will be addressed shortly.

2.4.7.2 Trace Oxygen

As previously mentioned, the presence of air in batch reactor pyrolysis studies is a considerable concern. Air which is trapped with the hydrocarbon in the reactor, or even dissolved in it, is often the cause of misleading results. Tubular–flow reactor studies have also been plagued with air contamination. Thus, a handful of studies (Niclause et al., 1967; Blakemore et al., 1973; Martin et al., 1976) have been conducted to determine the specific effects of trace oxygen on pyrolysis reactions. Specifically, alkanes ranging from ethane to isopentane have been pyrolysed at temperatures ranging from 500 – 600°C in the presence of small quantities of oxygen. All of the studies have been conducted at low conversion (less
than 1%) to minimize the interference of products.

The above mentioned studies have concluded that, depending on reactor surface effects, oxygen can either accelerate or, on the contrary, inhibit the pyrolysis of alkanes. For a relatively low surface/volume (S/V) ratio, oxygen accelerates the reactions. Whereas for higher S/V ratios (greater than 12 cm⁻¹) and/or lead oxide—coated glasses, the quantity of pyrolysis products is significantly reduced. For example, Blakemore et al. (1973) examined the pyrolysis of n—butane in a gold micro—reactor (530–600°C; 1 atm; S/V = 12.6 cm⁻¹) and found that trace quantities of oxygen present in the reaction system from 5 to 500 ppm had major inhibiting effects on the pyrolysis. When even 7 ppm of oxygen was present, typical butane pyrolysis products, such as methane, ethane, and propylene, were reduced by about 70% relative to pyrolysis in the absence of oxygen. As the oxygen concentration was increased, large quantities of ethylene, 1—butene, trans—2— butene, cis—2— butene, 1,3—butadiene and water were noted. In order to understand these results, one must delve into the free—radical chain mechanism.

When an alkane is pyrolysed in the presence of oxygen, new processes can appear which alter the free—radical chain mechanism (Martin et al., 1976).

(1) The pyrolysis reaction chain carriers can become oxidized and yield oxygenated free radicals, particularly HO₂⁺ and HO⁺. These radicals then propagate an alkane chain oxidation which competes with the alkane chain decomposition. For example, in the case of n—butane, the butenes and hydrogen peroxide/water would be formed as follows:

\[ \text{C}_4\text{H}_9^+ + \text{O}_2 \rightarrow \text{C}_4\text{H}_8 + \text{HO}_2^+ \]  \hspace{1cm} (2.25)

\[ \text{HO}_2^+ + \text{C}_4\text{H}_{10} \rightarrow \text{H}_2\text{O}_2 + \text{.C}_4\text{H}_9^+ \]  \hspace{1cm} (2.26)
\[ C_4H_9 \cdot \rightarrow C_4H_8 + H. \]  \hspace{1cm} (2.27)

\[ H \cdot + O_2 \rightarrow HO \cdot + O: \]  \hspace{1cm} (2.28)

\[ O: + C_4H_{10} \rightarrow HO \cdot + C_4H_9. \]  \hspace{1cm} (2.29)

\[ HO \cdot + C_4H_{10} \rightarrow H_2O + C_4H_9. \]  \hspace{1cm} (2.30)

The ethylene production increase is caused by a similar mechanism, employing an ethyl radical instead. The formation of 1,3-butadiene is attributed to subsequent oxidation of 1-butene.

The presence of oxygen may also cause a new initiation process:

\[ C_nH_{2n+2} + O_2 \rightarrow C_nH_{2n+1} \cdot + HO_2. \]  \hspace{1cm} (2.31)

Thus, additional free radicals are formed and an acceleration of the pyrolysis reactions results.

The presence of new oxygenated free radicals, however, also tends to make new chain termination processes appear. These oxygenated free radicals, unlike alkyl radicals, are easily destroyed on solid surfaces, especially when they are covered with lead oxide coatings. The net result is that chains which would normally lead to pyrolysis products are terminated. Thus, oxygen can also have an inhibiting effect on paraffin decomposition, which is intensified as vessel walls are larger (higher S/V) or covered with lead coatings.

The above mechanism has been verified by experiments on a number of paraffins (Martin et al., 1976). In particular, it was noted that olefins possessing the same number of carbon atoms as the feed were very dominant. Thus, for heavy paraffin pyrolysis, it would follow that the presence of oxygen would create an olefin that is otherwise not formed. (Recall that in the pyrolysis of a paraffin, \( C_nH_{2n+2} \), only 1-olefins in the range of 2 to \((n-1)\) carbon atoms are formed.) Thus, it should
be relatively easy to determine, based on the pyrolysis product distribution, whether oxygen was present during pyrolysis.

2.4.7.3 Reactor Surface

One feature of pyrolysis which is not fully understood is the role of the reactor surface. It has been demonstrated that factors such as the material of construction, surface to volume ratio of the reactor, and chemical treatment of the reactor surface often affect the rate of reaction and/or the product distribution. The inhibiting effect of trace oxygen, as discussed above, is just one of many surface reactions that affect pyrolysis. These reactions can be expected to be of even greater importance when smaller diameter (and hence higher S/V ratio) reactors, such as laboratory units, are employed.

At least seven surface reactions are thought to occur during most industrial pyrolysises. In a complex and, as yet, not completely understood manner, they all contribute directly or indirectly to coke formation. Coke formation in a pyrolysis unit is highly undesirable for several reasons: decreased yields of desired products, increased resistance of heat transfer to the reactants, and potential plugging of the reactor. Albright and collaborators (Dunkleman and Albright, 1976; Tsai and Albright, 1976; Brown and Albright; 1976) have proven that the surface reactions which accompany pyrolysis can produce metal oxides, coke, carbon oxides and hydrogen. The extent to which these reaction occurs depends on the composition of the inner surface of the reactor. Significant wall activity has been observed in reactors constructed of stainless steel, Incoloy and other alloys under operating conditions typical of commercial pyrolysis (800°C; 0.3 – 1.2 s). On the other hand,
Dunkleman and Albright have demonstrated, that glass (Vycor) reactor surfaces are relatively inert. Considerably higher yields of ethylene and no carbon oxides were obtained in a laboratory Vycor reactor as compared to those constructed of Incoloy 800 (high nickel and chromium content) and, especially, a 304 stainless steel. It is believed that the metal surfaces, especially nickel, promote secondary reactions such as the formation of aromatics from olefins through the Diels–Alder mechanism and subsequent dehydrogenation. As explained in Section 2.4.1.3, very complex polycyclic hydrocarbons, typical of coke, would then be produced on the reactor wall through further Diels–Alder/dehydrogenation reactions involving the aromatics and additional olefins. Albright and Yu (1979) have shown that the coke deposited on the Vycor glass surface or an alonized Incoloy 800 surface contained no metal and was inactive. However, the coke deposited on the Incoloy 800 surface was impregnated with metal atoms, such as iron or nickel, thus rendering it magnetic. These metal particles were found to catalyze further coke formation. Also, if steam was employed as a diluent, it then reacted with part of this magnetic coke to form carbon oxides (CO and CO$_2$) and more hydrogen.

Steam is also responsible for the formation of metal oxides on the reactor surface.

\[
\text{(metal)}_{\text{surface}} + \text{H}_2\text{O} \rightarrow \text{(metal oxides)}_{\text{surface}} + \text{H}_2 \quad (2.32)
\]

For example, the steam treatment of temperature–resistant Incoloy 800 at 800°C for 24 hours resulted in significant formation of NiO, Fe$_3$O$_4$ and hydrogen (Tsai and Albright, 1976). These metal oxides then reacted with hydrocarbons forming additional carbon oxides, water and hydrogen. These reactions caused a major reduction of the surface which, in the long term, severely weakened the metal.
2.5 n-HEXADECANE PYROLYSIS

As previously noted, the pyrolysis of pure paraffins, from pentane through to tetracosane, has been studied by numerous researchers over the past few decades. In particular, n-hexadecane has been the subject of research on numerous occasions, beginning with Voge and Good (1949). This is likely due to the fact that it is a compound fairly representative of gas oils. Most of the n-hexadecane pyrolysis studies have been conducted at temperatures ranging from 400 – 600°C, which is outside the industrial range of interest. Residence times have been in the order of one to several seconds; millisecond pyrolysis has only been reported once (Depeyre et al., 1985). As well, pressures have often exceeded atmospheric by up to 150 times; thus an entirely different product slate and distribution resulted. Voge and Good (1949), during 500°C n-hexadecane pyrolyses, observed that an increase in pressure from atmospheric to 21 atm caused a dramatic increase in conversion, increased saturation of the products and a general shift of products towards higher molecular weights. These observations are in accordance with the discussion of Section 2.4.1.5. However, as high pressure operation is not relevant to this research, as discussed in Section 2.4.1.5, these studies will not be discussed.

Since the pioneering study of Voge and Good (1949), the low pressure pyrolysis of n-hexadecane has been studied sporadically. However, with the increasing use of heavier pyrolysis feedstocks in the 1980’s, renewed attention has been focused on the pyrolysis of pure heavy hydrocarbons, including n-hexadecane. At the Laboratoire de Genie et Informatique Chimiques, Ecole Centrale des Arts et Manufactures (Malabry, France), simulation models for medium molecular weight hydrocarbon pyrolysis are currently under development. In particular, numerous
high temperature experiments have been conducted on n-hexadecane pyrolysis (Depeyre et al., 1985), the results of which are now being simulated. Other research institutes involved in similar research are EXXON Research and Energy Company (New Jersey) and the School of Chemical Engineering, Oklahoma State University (Stillwater, Oklahoma).

Tables 2.1 and 2.2 have been prepared to provide a clear comparison of the low pressure, vapor-phase n-hexadecane pyrolysis studies to date. Information regarding the reactors employed, operating conditions, and pyrolysis results are presented. The tabulated kinetic data correspond to a first order reaction assumption. Recently, Rebick (1981) confirmed that n-hexadecane pyrolysis is indeed approximately first order in n-hexadecane. At this time, an extensive discussion of the reaction systems employed will be presented.

2.5.1 Reaction Systems

All the n-hexadecane pyrolysis studies to date have employed tubular-flow reactors externally-heated by a regulated furnace. The more recent studies incorporated a feed preheater upstream of the reactor (Zhou et al., 1987; Depeyre et al., 1985; Rebick, 1981), so as to minimize the heat-up time in the reactor. Zhou et al and Rebick maintained the preheater at a fairly low temperature (less than 300°C) such that the feed was just vaporized. Depeyre et al., on the other hand, employed a rather hot 480°C. As well, these researchers recognized the importance of quenching the pyrolysis products. In each case, the reactor effluent was "immediately" passed through a series of air or ice traps in order to stop the reactions. Although far from rapid, this quenching technique is better than none at
### Table 2.1: Reported Low-Pressure n-Hexadecane Pyrolyses - Reactor Details

<table>
<thead>
<tr>
<th>Reference</th>
<th>Operating Conditions</th>
<th>Reactor</th>
<th>Type</th>
<th>Dimensions (mm)</th>
<th>S/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (deg. C)</td>
<td>Pressure (atm)</td>
<td>Rxn. time (s)</td>
<td>Diluent</td>
<td>Diameter Length (1/cm)</td>
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</tr>
<tr>
<td>Zhou et al (1987)</td>
<td>620</td>
<td>1.0</td>
<td>3.2</td>
<td>None</td>
<td>Concentric</td>
</tr>
<tr>
<td>Oklahoma State University; Stillwater, Oklahoma</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>304 SS tubes with preheat</td>
</tr>
<tr>
<td>Depeyre et al (1985)</td>
<td>600</td>
<td>1.0</td>
<td>n/a</td>
<td>Steam</td>
<td>Concentric</td>
</tr>
<tr>
<td>Ecole Centrale des Arts et Manufactures; Malabry, France</td>
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<td>1.0</td>
<td>n/a</td>
<td></td>
<td>Incoloy tubes</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>1.0</td>
<td>n/a</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>1.0</td>
<td>n/a</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.0</td>
<td>n/a</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>1.0</td>
<td>n/a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rebick (1981)</td>
<td>502</td>
<td>0.18</td>
<td>20.9</td>
<td>Nitrogen</td>
<td>Quartz tube</td>
</tr>
<tr>
<td>EXXON Research; Linden, New Jersey</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>with preheat</td>
</tr>
<tr>
<td>Groenendyk et al (1970)</td>
<td>517</td>
<td>n/a</td>
<td>1.21-3.46</td>
<td>Helium</td>
<td>Gold-plated tube</td>
</tr>
<tr>
<td>Hewlett-Packard Company; Avondale, Pennsylvania</td>
<td>553</td>
<td>n/a</td>
<td>1.16-3.31</td>
<td></td>
<td>tube</td>
</tr>
<tr>
<td></td>
<td>583</td>
<td>n/a</td>
<td>1.12-3.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Panchenkov &amp; Baranov (1958)</td>
<td>520</td>
<td>1.0</td>
<td>n/a</td>
<td>n/a</td>
<td>tube</td>
</tr>
<tr>
<td>U.S.S.R.</td>
<td>550</td>
<td>n/a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>n/a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voge &amp; Good (1949)</td>
<td>500</td>
<td>1.0</td>
<td>118</td>
<td>None</td>
<td>SS tube</td>
</tr>
<tr>
<td>Shell Development Company; Emeryville, California</td>
<td>211</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Note: n/a - not available
### Table 2.2: Reported Low-Pressure n-Hexadecane Pyrolyses - Results

<table>
<thead>
<tr>
<th>Reference</th>
<th>Operating Conditions</th>
<th>Results</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. (deg. C)</td>
<td>Pressure (atm)</td>
<td>Rxn. time (s)</td>
<td>n-C16 Conv. (%)</td>
</tr>
<tr>
<td>Zhou et al (1987) Oklahoma State University;</td>
<td>620</td>
<td>1.0</td>
<td>3.2</td>
<td>39.5</td>
</tr>
<tr>
<td>Stillwater, Oklahoma</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depeyre et al (1985) Ecole Centrale des Arts</td>
<td>600</td>
<td>1.0</td>
<td>n/a</td>
<td>41.8</td>
</tr>
<tr>
<td>Malabry, France</td>
<td>650</td>
<td>n/a</td>
<td></td>
<td>75.2</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>n/a</td>
<td></td>
<td>92.9</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>1.1</td>
<td></td>
<td>99.0</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.0</td>
<td></td>
<td>99.2</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>0.8</td>
<td></td>
<td>98.6</td>
</tr>
<tr>
<td>Rebick (1981) EXXON Research; Lindon, New Jersey</td>
<td>502</td>
<td>0.18</td>
<td>20.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Groenendyk et al (1970) Hewlett-Packard Company;</td>
<td>517</td>
<td>n/a</td>
<td>1.21-3.46</td>
<td>0.3-1.5</td>
</tr>
<tr>
<td>Avondale, Pennsylvania</td>
<td>553</td>
<td>1.16-3.31</td>
<td></td>
<td>2.0-5.9</td>
</tr>
<tr>
<td></td>
<td>583</td>
<td>1.12-3.19</td>
<td></td>
<td>6.6-19.0</td>
</tr>
<tr>
<td>Panchenkov &amp; Baranov (1958) U.S.S.R.</td>
<td>520</td>
<td>1.0</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>550</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>580</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voge &amp; Good (1949) Shell Development Company;</td>
<td>500</td>
<td>1.0</td>
<td>118</td>
<td>31.5</td>
</tr>
<tr>
<td>Emeryville, California</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: (a) recalculated using Benton (1931) rate constant equation
n/a not available
As previously discussed in Section 2.2.2, small diameter reactors should be employed in order to minimize the radial thermal and mass transfer gradients. Under these guidelines, only Groenendyk et al. (1970) utilized a reactor of sufficiently small diameter. Thus, unlike the others, they can rightly state that pyrolysis occurred under isothermal conditions. Zhou et al., Depeyre et al., Rebick, and Voge and Good (1949) realized that, due to the "larger than optimum" diameter of their reactors, the reactor wall temperature may be far greater than the actual reaction temperature. Thus, radial thermal gradients would be unavoidable. As stressed earlier, accurate knowledge of the actual reaction temperature is critical to the attainment of valid kinetic data. Consequently, Voge and Good controlled the temperature of the center of the tube rather than the wall. Likewise, the others employed reactors consisting of concentric tubes. The reaction was conducted in the annular space, whilst a Type K thermocouple, placed in the inner tube (sheath), measured the actual reaction temperature. Rebick demonstrated that if the reaction tube diameter is, say, 10 mm or smaller, not only are there no radial thermal gradients but the temperatures are also fairly constant along the length of the reactor. Consequently, there was no need for an inner thermocouple as the reaction occurred under near–isothermal conditions.

It is obvious, by now, that past researchers have employed diverse reactor configurations. Various materials of construction have been utilized as well. Zhou et al. and Voge and Good both employed stainless steel reactors. However, because steam was not employed in either study, it is unlikely that surface effects played a major role. Nevertheless, Voge and Good pre–treated the reactor surface and
subsequently found no evidence of catalysis. Rebick (1981) and Groenendyk et al. (1970) utilized quartz and gold-plated reactors, respectively, to positively eliminate the occurrence of surface reactions. Depeyre et al. (1985) utilized both Incoloy and quartz reactors, thus allowing them to readily determine the effect of the Incoloy surface. As well, they employed steam as a diluent, in an effort to better simulate industrial cracking. Since steam was present and the S/V ratio of the Incoloy reactor was quite high, it is likely that surface reactions played a significant role.

2.5.2 Operating Conditions

The previous section has highlighted the fact that reaction temperature in a flow reactor is not an easily controlled nor known quantity. As well, residence (reaction) times are not directly measurable. Consequently, some degree of caution should be exercised when reviewing the operating conditions listed in Table 2.1.

Of the six studies listed in Table 2.1, only the two most recent (Zhou et al. and Depeyre et al.) quote temperatures within the industrial range of 600–850°C. All other studies have been conducted at lower temperatures, ranging from 500 to about 580°C. As noted above, the Zhou et al. and Depeyre et al. reactors likely exhibited both radial and axial temperature gradients. There is no doubt that the temperatures listed in Table 2.1 correspond to those determined by the thermocouple located at the inner wall of the reactor. However, there is no way of knowing the axial position of these measurements. Thus, the temperatures given by these studies cannot be trusted. Such is not the case for the other studies. Rebick and Groenendyk conducted their experiments in reactors proven to be isothermal. Although Voge and Good's reactor was larger than optimum, they stated that the
temperature control in the center of the tube was within \( \pm 3^\circ C \) of the specified value. Consequently, the temperatures given by the latter three studies are thought to be highly accurate.

Table 2.1 reveals that only Depeyre et al. have conducted pyrolyses at reaction (residence) times of less than 1 second. However, before the other studies are discounted, a brief discussion of the problems associated with the determination of the actual residence time is in order. Strictly speaking, the residence time, \( t_r \), in a flow reactor depends on the extent to which the volume changes during the progress of the reaction, assuming the flow rate, \( v_0 \), of the entering gases is maintained constant. Stated mathematically,

\[
t_r = \int_0^z \frac{A \ dz}{v(z)} \tag{2.33}
\]

where, \( A \) represents the reactor cross-sectional area and \( z \) the reactor length. Usually, the flow rate as a function of reactor length, \( v(z) \), is not known. Thus, most researchers choose to state the space time, labelling it incorrectly as the residence time. The space time, \( \tau \), is merely the reactor volume, \( V \), divided by the flow rate of the entering gases, \( v_0 \), assuming isothermal reaction conditions. The equivalent reactor volume concept (Hougen and Watson, 1947) is often employed to convert non-isothermal reaction data to a pseudo-isothermal basis, despite its shortcomings. The equivalent reactor volume obtained in then used to determine the space time. Only in the case where the flow rate through the reactor is constant (equimolar, isothermal reaction), are the space time and residence time equivalent. As the total number of moles always increases with conversion in vapor-phase pyrolysis, one must realize that the space time will always exceed the actual residence time.
Of the studies presented in Table 2.1, all reaction times quoted are, in fact, space times. Unfortunately, Zhou et al. did not correct for non-isothermicity; consequently, the space times given are incorrectly high. Depeyre et al. did employ the equivalent reactor volume concept. However, it was used improperly; rather than choose a reference temperature corresponding to the mean reaction temperature in the last 40% of the reactor, as suggested by Van Damme et al. 1975), they utilized the furnace (reactor wall) temperature. Consequently, the equivalent reactor volume predicted would be incorrectly low, as would the space time. A further error was identified in the Depeyre et al. space time determination; they employed the outlet rather than the inlet flow rate. This too caused an underestimation of the space time. There is no doubt that Depeyre et al. have made several errors, which, in the end, will affect not only the stated operating conditions but also the kinetic parameters as well. Unfortunately, there was not sufficient information available to permit recalculation of the data.

2.5.3 Kinetic Results

Various reactor configurations and operating conditions have been employed in past n-hexadecane pyrolysis studies. Thus, one would expect a fair amount of variability in the resulting data. A simple Arrhenius plot (natural logarithm of the first order rate constant versus inverse temperature) can be generated to allow comparison of the data. For a first order reaction in a constant volume reactor, the following expression is employed to determine the rate constant, \( k \):

\[
k = \frac{1}{t_r} \ln \frac{1}{1 - x}
\]

where \( x \) refers to the fractional conversion of the feed. Frequently in publications,
the space time, which does not account for the increase is moles due to reaction, is quoted rather than the actual residence time, $t_r$. However, as mentioned previously, they are not equivalent. Consequently, whenever space time, $\tau$, is used in conjunction with equation (2.34), serious underestimation of the rate constant, particularly at high conversions, occurs. Rather, an equation proposed by Benton (1931) should be employed when analyzing flow reactor data characterized by a space time.

$$\text{A} \rightarrow \nu \text{B}$$

$$k = \frac{1}{t_r} \left[ \nu \ln \left( \frac{1}{1 - x} \right) - (\nu - 1) x \right]$$

The first order rate constant, $k$, is a function of the number of moles of product per mole of n–hexadecane pyrolysed, $\nu$, as well as the conversion, $x$, and residence time, $t_r$. The kinetic data of Zhou et al. required recalculation using this equation; the rate constants which appear in Table 2.2 are the recalculated values. The Groenendyk et al. (1970) kinetic data was also not calculated using equation (2.36); however, at the low conversions experienced, the error is not significant. As well, there was insufficient product distribution data to permit recalculation.

Using data from Table 2.2, an Arrhenius plot has been generated and appears as Figure 2.1. This figure indicates, surprisingly enough, fairly good agreement among the studies. Of the three studies conducted at more than one temperature (Depeyre et al.; Groenendyk et al.; and Panchenkov and Baranov), all possess slopes that are approximately equal, indicating activation energies of approximately 57 kcal/mol. As very little information was available on the Panchenkov and Baranov study, the data should not be heavily relied upon. The Depeyre et al. data is
Figure 2.1: n–Hexadecane Pyrolysis — Reported Kinetic Data

- ○ = Zhou et al.
- △ = Depeyre et al.
- + = Rebick
- × = Groenendyk et al.
- ◊ = Voge & Good
- ▽ = Panchenkov & Baranov
positioned somewhat higher than predicted by extrapolation of the low temperature data; this is likely caused by the erroneous determination of the space times. The leveling of the Depeyre et al. data at temperatures greater than 700°C is caused by inhibition. As this data was gathered from quartz reactor pyrolysis runs, there is no worry of enhanced secondary reactions due to surface effects. The Groenendyk et al. curve may be slightly low because the minor increase in moles due to reaction was not considered. The single temperature studies of Zhou et al., Voge and Good, and Rebick fit in well with the rest of the data.

The kinetic data for past n-hexadecane pyrolyses have agreed quite well, with the possible exception of the Depeyre et al. study. However, as this is the only study which really covers the range of interest, it cannot be totally discounted, but rather should be analyzed cautiously.

2.5.4 Effect of Temperature and Reaction Time on Conversion

Temperature and/or reaction time can have a dramatic effect on pyrolysis reactions. An examination of the data presented in Table 2.2 clearly exemplifies this fact. Depeyre et al. (1985) pyrolysed n-hexadecane at approximately 600 to 850°C for approximately one second and obtained conversions ranging from 41.8% to 99.2%. The fact that the conversions are so high and the space times quite low is indicative of how fast the reactions become when temperatures exceed 650°C. On the other hand, pyrolysis is a very slow reaction at 500°C. Rebick pyrolysed at 500°C for a lengthy 20.9 s and only converted 4.9% of the feed. Voge and Good pyrolysed at 502°C for a very lengthy 118 s and obtained a conversion almost 10 times greater than that of Rebick. However, the conversion was comparable to that
achieved by Depeyre et al. at 600°C and approximately one second. The conversions achieved by the Depeyre et al. 600°C run and the Zhou et al. 620°C, 3.2 run are comparable. This fact proves that the Depeyre et al. space times have been severely underestimated.

2.5.5 Product Distributions

Product yields versus n–hexadecane conversion have been plotted in Figure 2.2 in an attempt to allow proper comparison of data from all the studies. For obvious reasons, a plot of product yields versus reaction, or even space, time would be pointless. In an effort to minimize confusion, the products have been grouped as follows: hydrogen/methane, ethylene, other gases \( \left(C_4^-\right) \), \( C_5^-C_9 \) 1–olefins, \( C_{10^-C_{15}} \) 1–olefins and, finally, aromatics. The "other gases" fraction includes ethane, propylene, propane, butenes, and 1,3–butadiene, if present. The two 1–olefin fractions include the entire range of 1–olefins; these were detected in all the studies. As product distribution data was not available for the Groenendyk et al. nor the Panchenko and Baranov studies, these are not represented with the others on the figure. The conditions employed by the various researchers, as taken from Table 2.2, are:

- Rebick
  - 502°C; 20.9 s space time
- Voge and Good
  - 500°C; 118 s space time
- Zhou et al.
  - 620°C; 3.2 s space time
- Depeyre et al.
  - 600–750°C; space times incorrect

The data reported for the Depeyre et al. study corresponds to that generated in the quartz, rather than the Incoloy reactor. As well, the 800 and 850°C Depeyre et al. data have not been presented due to space restrictions on the figure.
Figure 2.2: n-Hexadecane Pyrolysis
Reported Product Distributions

- $\bigcirc = H_2/CH_4$
- $\bigtriangleup = C_2H_4$
- $+ = \text{other gases}$
- $\times = C_5-C_9 \text{ 1-olefins}$
- $\diamond = C_{10}-C_{15} \text{ 1-olefins}$
- $\nabla = \text{aromatics}$
Fairly definite trends are displayed in Figure 2.2. As conversion is increased from a mere 4.9% to 99.0%, significant changes in the product distribution occur. At very low conversions (Rebick, 1981), only \( C_1 \) to \( C_3 \) paraffins and the entire range of \( 1 \)-olefins from ethylene through to pentadecene were produced, as predicted by the Rice–Kossiakoff theory. The \( C_{10}-C_{15} \) 1-olefins accounted for more of the product stream than did the lighter \( C_5-C_9 \) 1-olefins. In fact, the yields increased as the carbon number increased, with the exception of 1-pentadecene. This indicates that the heavier olefins had not yet decomposed into lighter species. The fact that no aromatics were detected is further proof that the reaction was still in its early stages. As well, the gas yields were fairly low, with ethylene only accounting for 0.5 wt%. The other major gas products were, in order of decreasing prevalence: propylene, ethane, 1-butene, methane and propane.

As the conversion is increased to 31.5% (Voge and Good, 1949), the yields of all product groups increase. However, the product distribution is somewhat varied from that of Rebick. Especially peculiar are the large yields of gases other than hydrogen/methane/ethylene and simple aromatics (benzene and toluene). These "other gases" were primarily composed of propylene, ethane, 1-butene and propane. Although not shown, 1 wt% coke was also formed. The lengthy space time (118 s) likely caused the over-production of these components. As well, the especially large ethane and propane yields would lead one to believe that radical decomposition was rapidly occurring, thus producing plenty of small radicals that would then stabilize through hydrogen abstraction to form light paraffins. As should be expected at this moderate conversion, the \( C_{10}-C_{15} \) 1-olefins were still more prevalent than the lighter \( C_5-C_9 \) 1-olefins. As well, the ethylene and methane/hydrogen product yields are in line with data points following at higher conversions. Although not
indicated on the plot, 1,3-butadiene and isomerized olefins were detected in addition to the full range of C₂ to C₁₅ 1-olefins, C₁ to C₃ paraffins, hydrogen, simple aromatics, and coke.

Zhou et al. pyrolysed n-hexadecane at 620°C, 3.2 s in a sizable stainless steel tubular reactor and achieved a 39.5% feed conversion. The product distribution which resulted, however, does not agree with the data of other researchers, such as Depeyre et al. (600°C pyrolysis; 41.8% conversion). As a stainless steel reactor was employed in the Zhou et al. study, it is likely that surface effects are responsible for the very large "other gases" and correspondingly low C₁₀–C₁₅ 1-olefins production. This large gas fraction is once again primarily composed of propylene, 1-butene and ethane; the propane peak was not resolved from propylene. As seen with the Voge and Good data, the ethylene and methane/hydrogen yields are fairly in line with data of lower and higher conversion. Once again, the most dominant products were, in decreasing order of prevalence, ethylene, methane, propylene, ethane and butene; hydrogen was only detected in small quantities. Unlike the Voge and Good study, however, the lighter C₅–C₉ 1-olefins were far more prevalent than the less stable C₁₀–C₁₅ 1-olefins. The full 1-olefin series was detected; however, the 1-pentadecene yield was noticeably low, as also observed by Rebick. In addition to the 1-olefins, a series of isomers ranging from C₅ to C₁₃ were detected. These isomers likely consisted of isomerized olefins, diolefins and even cyclic olefins. A severe inconsistency in the data is the absence of reported aromatics, while coke yields are listed at approximately 1 wt%.

Despite the fact that the space times were incorrectly determined, the Depeyre et al. (1985) publication is likely to be the most useful due to the fact that
they pyrolysed n-hexadecane at temperatures of interest. As mentioned above, the data presented in Figure 2.2 corresponds to runs conducted in a tubular quartz reactor from 600 to 750°C, with conversions of 41.8 – 99.2%, respectively. The results of the 800 and 850°C runs, although not included on Figure 2.2 due to space restrictions, will also be discussed at this time. Before proceeding further, consideration should be given to the fact that Depeyre et al. employed a poor quench system. Consequently, the conversions exhibited at the higher temperatures, where reactions occur very quickly, are likely higher than those that would be obtained in a properly designed reaction system. As well, Depeyre et al. employed a rather hot feed preheat section; this would also cause enhanced conversions.

Very definite trends are displayed in Figure 2.2. For example, as the conversion level proceeded from moderate (41.8%) to extreme (99.2%), significant increases in the gas production (hydrogen/methane, ethylene and "other gases") occurred. As well, aromatics production increased significantly from zero at 41.8% conversion (600°C). In fact, at 850°C, the aromatics accounted for a startling 21 wt% of the products. These upward trends were accompanied by a general decline in the 1-olefins production; in fact, at the 99% conversion level, no 1-olefins remained. Thus, it is obvious that secondary reactions played a very significant role in the Depeyre et al. experiments, particularly at the higher temperatures.

Further examination of the Depeyre et al. data indicates that the maximum C_{10} - C_{15} 1-olefin content was achieved at a low conversion (41.8% – 600°C). On the other hand, the C_{5} - C_{9} 1-olefins peaked at 650°C (75.2% conversion). As shown in Figure 2.2, the "other gases" yield reached a maxima at 92.9% conversion.
(700°C), whereas the hydrogen/methane and ethylene fractions continued to increase with higher conversion. The late decline of the "other gases" yield is attributed to decomposition of the butenes, propylene and, even, 1,3-butadiene. At temperatures greater than 750°C and conversions greater than 99%, the ethylene yield did, in fact, start to decline, indicating the complete domination of secondary reactions at very high conversions. As these declines were accompanied by a large production of aromatics, it is likely that these aromatics formed through a Diels–Alder mechanism involving ethylene/propylene and 1,3-butadiene, as suggested in Section 2.4.1.3. In fact, intermediate cyclic diolefins, such as cyclohexadiene, were detected. Among the aromatics, benzene, toluene, styrene, indene and, especially, naphthalene were very prominent. The more complex polyaromatics and alkylated aromatics were also noted. As well, acetylene was detected in small quantities (2 wt%) at the high conversion (greater than 99%), high temperature (greater than 750°C) runs conducted.

Depeyre et al. also pyrolysed n-hexadecane in an Incoloy reactor in an attempt to determine the effect of the metal surface on the pyrolysis reactions. For n-hexadecane conversions of less than 50%, similar experimental results were obtained with the Incoloy and quartz reactors. However, at higher conversions, pyrolyses in the Incoloy reactor produced large quantities of hydrogen and aromatics and coke was deposited on the reactor walls. For example at approximately 80% conversion (700°C), the aromatics yield obtained from an Incoloy reactor run was four times higher than that obtained from a comparable quartz reactor run. As noted in Section 2.4.7.3, high aromatics and non-zero coke production is attributed to the metal surface which likely promotes polymerization of the light 1-olefins as well as cyclo-addition of olefins by the Diels–Alder mechanism.
2.5.6 Reaction Modeling

The free–radical Rice–Kossiakoff mechanism has been employed by Depeyre et al., Rebick, and Voge and Good in an attempt to simulate the product distributions of \( n \)-hexadecane pyrolysis. This is not a small task; the mechanism applied to \( n \)-hexadecane includes at least 90 reactions, all of which are primary reactions and most of which account for radical isomerization. It is likely that these researchers have, in some way, simplified the model by eliminating some of these reactions. However, few details are given in their publications. A detailed description of the Rice–Kossiakoff model applied to \( n \)-decane pyrolysis does, however, exist (Billaud and Freund, 1986).

For pyrolyses conducted at low temperatures (less than 650°C) and low conversions (less than 20%), good agreement was displayed between experimental and predicted distributions (Depeyre et al.; Rebick). At these conditions, secondary reactions were largely absent. Thus, the Rice–Kossiakoff model, which only accounts for primary products, no doubt matched quite well. However, once the conversion level exceeded 20%, the predicted values started to deviate significantly from the experimental data. The decomposition of 1-olefins and formation of dienes and aromatics were not predicted, while the ethylene yields were over–predicted.

It is fairly obvious that for conditions within the Ultrapyrolysis regime (greater than 700°C), application of the Rice–Kossiakoff reaction mechanism would be futile, unless conversions were limited to 20%. The secondary reactions, described in Section 2.4.1.3, must be incorporated along with the Rice–Kossiakoff mechanism to form a model capable of accurately predicting the product
distributions of high conversion pyrolysis. Unfortunately, there is no evidence of such a model within the published literature. However, these models no doubt exist, though unpublished for proprietary reasons.
CHAPTER 3 – RESEARCH OBJECTIVES

Tremendous advancements have been in made in pyrolysis technology over the past decade. By moving to high temperatures and short reaction times, typical of Ultrapyrolysis, significant increases in ethylene yield have been obtained. As well, the technology has proven to be very versatile; feeds ranging from ethane through to heavy gas oil (Dluzniewski et al., 1981) have been successfully pyrolysed using a similar reactor design. However, with the exception of the light paraffins (such as ethane and propane), the pyrolysis reactions are not well understood, particularly within the Ultrapyrolysis regime. For the most part, only global kinetic data with no accompanying reaction mechanism has been reported for feedstocks such as gas oil and whole crude. In order to better understand the pyrolysis of such feeds, the response of the individual components in these feeds to pyrolysis must first be understood. Thus, the pyrolysis of n—hexadecane will be studied with the intent of gaining a valuable insight into gas oil pyrolysis.

In particular, the objectives of this study are:

(1) Implementation of a micro—reaction system capable of operating under conditions typical of Ultrapyrolysis. Specifically, the system must permit rapid heating to a high temperature, maintenance of this temperature for a very short duration, and rapid quenching of the pyrolysis products. Curie point pyrolysis is proposed.

(2) Employment of this micro—reaction system to pyrolyse n—hexadecane at temperatures ranging from 600 to 850°C and reaction times of 100 milliseconds to several seconds. Catalytic effects will also be
investigated.

(3) Design and implementation of a gas chromatography system capable of resolving the many pyrolysis products.

(4) Determination of the pyrolysis kinetics of n-hexadecane, assuming a first-order reaction. The long reaction time (greater than 500 ms) data will be compared to literature values, in an attempt to validate the experiments.
CHAPTER 4 – EXPERIMENTAL PROGRAM

4.1 APPARATUS

4.1.1 Equipment Design

The pyrolysis reaction system employed in this study has been designed to both accommodate the study of n-hexadecane Ultrapyrolysis and the determination of its intrinsic kinetics. To satisfy the first objective, the system must be capable of rapidly heating to a very high pyrolysis temperature, which is maintained for only a very short time before rapid quenching of the reaction products is initiated. To successfully determine the kinetics of n-hexadecane pyrolysis, the reactor must also be designed so as to eliminate the possibility of mass and heat transfer gradients, contaminants (eg. oxygen) and catalytic reactor surfaces. If the reactor and sample sizes are kept small, concentration and temperature gradients will be negligible. Finally, the pyrolysis should be conducted at a precisely known temperature and reaction time.

An innovative micro-reaction system, which satisfies the above criteria, has been employed to study the pyrolysis of n-hexadecane. In short, a small glass batch reactor, containing microgram quantities of n-hexadecane (termed the 'micro-reactor') is brought quickly to a pre-defined temperature by a Curie point pyrolyser. The pyrolysis timing is carefully controlled by a timer control unit which is both responsible for starting the Curie point pyrolyser and activating a hammer which crushes the batch reactor, thus releasing the products to a helium gas stream;
rapid quenching results. The products are then swept immediately into a sophisticated gas chromatograph for analysis. A schematic representation of the equipment is shown in Figure 4.1. As well, photographs of the entire apparatus (Figure 4.2) and the micro-reaction system/timer control unit (Figure 4.3) are included for clarity. In Figure 4.2, the Varian 401 Chromatography Data System is situated in the foreground, followed by the Curie point pyrolyser control unit and the Varian 6000 Gas Chromatograph. The micro-reaction system, less the pyrolysis reactor module, is sitting atop the pyrolyser control unit. Both the timer control unit and the reactor module are likewise atop the gas chromatograph.

4.1.1.1 Micro-reactor

In conventional Curie point pyrolyser operation, a ferromagnetic wire, coated with a relatively nonvolatile reactant at the bottom end, is held in a pyrolysis chamber through which a continuous stream of carrier gas passes. As the wire is heated to its Curie point and pyrolysis occurs, the products are quenched as they rapidly expand away from the hot wire into the much cooler gas stream. The gas stream is often a few hundred degrees Celsius as the pyrolysis chamber is maintained fairly hot to ensure that the products pass to the gas chromatograph, rather than condensing on the chamber walls. There are two problems with this type of operation. First, as the pyrolysis chamber is heated, only those hydrocarbons with a boiling point much higher than the heater temperature will remain affixed to the wire. This restricts one to the study of very high boiling compounds. Second, as the pyrolysis products are not contained within the hot zone but rather freely pass into the carrier gas stream, there is no control on the reaction time. Both of these problems are clearly unacceptable in this study. However, a
Figure 4.1: Pyrolysis Apparatus Flow Chart
Figure 4.2: Pyrolysis Apparatus
Figure 4.3: Micro-reaction System / Timer Control Unit
simple solution has been found.

Rastogi (1987), in his work on propane pyrolysis, devised a modified Curie point pyrolysis technique. Rather than leave the coated ferromagnetic wire open to the carrier gas, he enclosed essentially that portion of the wire that is coated with the reactant in glass. Thus, a batch micro-reactor was formed. This micro-reactor was then simply placed in the bottom of the pyrolysis chamber (Figure 4.4). High-frequency (radio wavelength) heating of the short wire to its Curie point, and thus pyrolysis, still occurred, providing the pyrolysis chamber was of the proper length. As mentioned above, the pyrolysis products were released, at the end of a pre-set reaction time, through breakage of the micro-reactor. The pyrolysis chamber was dimensioned such that the wire would sit within the hot zone of the high frequency induction coil. The location of this zone was indicated by a discoloration of the ferromagnetic wire. The zone was, in fact, only 25 mm long.

The configuration of a typical micro-reactor is shown in Figure 4.5. The reactor is just over 12 mm long with a 0.15 mm gap between the 0.4 mm diameter wire and the inner glass surface. The detailed construction procedure is given in Appendix A. However, a brief discussion will be given here. A pre-cleaned 12 mm long ferromagnetic wire of predetermined Curie point temperature was coated with a n-hexadecane/carbon disulfide solution. The wires were cleaned using a procedure recommended by Gutteridge et al. (1984). The n-hexadecane was 99.42 wt% pure, as determined by gas chromatographic analysis. Carbon disulfide was employed to dilute the reactant so that a reasonably large volume could be evenly coated on the wire. The carbon disulfide then readily evaporated to leave approximately 15 μg of n-hexadecane remaining on the wire. The coated wire was
Figure 4.4: Micro-reactor in Place
Figure 4.5: Micro-reactor Configuration

FERROMAGNETIC WIRE (COATED WITH n-C16)

PYREX CAPILLARY
then inserted in a Pyrex capillary tube (0.7 mm ID x 0.87 mm OD), and quickly flame-sealed under vacuum. Evacuation was essential since no air may be present in the micro-reactor.

In the current study, micro-reactors were constructed with ferromagnetic wires of 600, 750 and 850°C nominal Curie point temperature. As well, some 750°C gold-plated wires were employed, with the intention of determining the difference between pyrolysis results, if any, from a suspected active metal surface and an inert reactor surface. D’erik Gold and Silversmith (Calgary) employed electroplating to apply a very thin gold layer, as recommended by Egsgaard and Carlsen (1983). The layer was approximately 64 nm thick, as determined by weighing.

4.1.1.2 Curie Point Pyrolyser

The Curie point pyrolyser employed is a commercial unit (Fischer Model 0316), which has been designed in accordance with the work of Simon and Giacobbo (1965), Bühler (1971) and Oertli (1974). As noted in Figure 4.1, the pyrolyser system consists of two components: the control unit and the interconnected pyrolysis reactor module. The pyrolyser is intended as a pre-injection system for a gas chromatograph. Thus, the control unit is placed next to the gas chromatograph to facilitate easy access of the gas chromatograph to the pyrolysis reactor module, which is placed atop the gas chromatograph injection block and secured by an adapter ring (Figure 4.2). A detailed schematic representation of the pyrolysis reactor module and accompanying hammer system appears in Figure 4.6. The supports have been omitted for simplification.
Figure 4.6: Micro-reaction System
Number Key — Figure 4.6

1. Pyrolysis chamber
2. Carrier gas switch—over valve
3. Hammer
4. Permanent magnet
5. Hammer—activating solenoid
6. Micro—switch
7. Induction coil in aluminum housing
8. Resistance heater
9. Gas chromatograph injection block
10. Induction coil power supply
11. Heater power supply
12. Heater sensor
13. Adapter ring
The pyrolysis reactor module is composed of many parts. The pyrolysis chamber (1), which is equipped with a needle, holds the micro-reactor and facilitates flow of helium carrier gas through to the gas chromatograph. The chambers supplied with the Fischer unit have not been employed. Rather, new chambers have been designed and built at The University of Calgary. A glassblower constructed the approximately 90.5 mm long borosilicate pyrolysis chambers and then fused them onto 87 mm long 22 gauge needles. Torr-seal (Varian) was then applied to the fused zone to provide added strength and an absolute seal. The chambers are dual diameter; the top 40 mm is 1/4" OD, while the rest of the chamber is 1/8" OD. The needle points have also been specially fashioned as plugging of the commercial needle points occurred when they were passed through the gas chromatograph injection port septum. The in-house needle points have a short tapered zone (approximately 1.5 mm length) which is curved upwards at the tip.

As seen in Figure 4.6, the pyrolysis chamber is connected, at its top, to a tee. The side-arm of this tee connects to the helium source line. This line is supplied by the gas chromatograph helium carrier gas line, through a solenoid—activated valve (2). The switch which activates the valve is located on the front panel of the control unit. The top of the tee permits access of the long rod—like hammer (3) into the pyrolysis chamber. It has been carefully sealed using a septum and specially—fashioned washers. The hammer is attached at its top to a permanent magnet (4), which is drawn downwards when a solenoid (5) is energized. The micro-switch (6) contacts the magnet at the end of its downward stroke.

The pyrolysis chamber is tightly encircled by an induction coil (7)/heater
combination. The induction coil is the source of high frequency heating to the ferromagnetic wire encased in the micro-reactor. An induction field of 1170 oersted and 480 kilohertz frequency is created. As previously mentioned, the efficient heating zone of the coil is a mere 25 mm long, compared to a total coil length of 55 mm. The coil is itself encircled by a resistance heater which is capable of maintaining the entire arrangement to a maximum set-point temperature of 311°C (actual temperature: 275°C). At this temperature, the n-hexadecane will be completely vaporized. Since the gas chromatograph injection block (9) is heated to a similar temperature, the possibility of condensation of the pyrolysis products on the pyrolysis chamber and/or needle walls is remote. Thus, one can be assured that the complete pyrolysis product stream reaches the analytical stage.

The control unit supplies the power (10) to the induction coil, which facilitates the high frequency heating of the pyrolysis reactor. It has been designed so as to maximize the heat-up rate of the reactor. Thus, in keeping with the findings of Oertli (1974), two stage power is employed. An initial impulse of 4.0 kW brings the ferromagnetic wire to temperature quickly, while a constant power input of 1.0 kW sustains the pyrolysis temperature. The control unit is also capable of controlling the pyrolysis start and duration, as well as the heater temperature.

4.1.1.3 Timer Control Unit

In an attempt to automate the Curie point pyrolyser start, pyrolysis duration and hammer drop, a timer control unit was designed (Rastogi, 1987). In particular, the unit takes into account the total time associated with the various steps of the hammer drop, from the activation of the hammer solenoid to the actual breaking of
the micro-reactor. When pyrolysis times are so short, the elapsed time (approximately 19 ms) for these incidents cannot be neglected. As well, the unit measures and displays the actual pyrolysis time, which can vary from the set time.

The configuration of the timer control unit is shown in Figure 4.7. It consists of a power switch, a safety switch, a trigger switch, two timer wheels (A—left and B—right), and, finally, a time display counter with a reset switch. The power switch is self-explanatory. The safety switch was recently installed to prevent accidental triggering of the timer control unit by suspected static. The trigger switch activates the delay timers A and B. The purpose of delay timer B is to offset the response time of the hammer system by starting the Fischer Curie point pyrolyser and the display counter, after an initial delay. A delay of 19 ms, equivalent to the average hammer system response time, was set on the timer wheel. The purpose of delay timer A is to control the desired pyrolysis time by turning on the hammer solenoid at the end of the programmed time. The hammer solenoid, in turn, causes the hammer to drop which, in turn, causes a micro-switch to be activated. The micro-switch was set so that it was activated at the moment when the micro-reactor was broken by the falling hammer. This switch stops the display counter so that the actual pyrolysis time is displayed. Often the actual pyrolysis time was up to 7 ms less than the set time.

4.1.1.4 Gas Chromatography System

"Analysis of the products of hydrocarbon pyrolysis represents one of the most difficult challenges in commercial chemistry (Willis, 1972)." Although 16 years have passed since this statement was written, it is still just as true today!
Figure 4.7: Timer Control Unit Schematic
Depending on the pyrolysis conditions, the product stream from a n-hexadecane pyrolysis may contain anywhere from trace to major quantities of very volatile gases, such as hydrogen and methane, to very high-boiling polyaromatics, such as phenanthrene and pyrene. An added complication is the fact that the pyrolysis products are transferred directly from the pyrolysis zone to the gas chromatograph. This dictates that the entire gas phase product spectrum must be analyzed in one sweep. However, according to Van Camp et al. (1983), direct analysis of the pyrolysis products in the gas phase is preferred as errors due to sample loss are then negligible. Obviously a very complex gas chromatography system must be implemented to enable resolution and quantification of all the product peaks. At present, no one chromatographic column is capable of resolving the entire pyrolysis product spectrum.

In order to conduct such a complex analysis, a sophisticated gas chromatograph and accompanying computer must be available. A gas chromatograph/mass spectrometry system is preferred. However, for pure hydrocarbon feeds, such as n-hexadecane, a gas chromatograph with several detectors will do the job. In the current study, a Varian 6000 gas chromatograph (GC) and its accompanying Varian 401 (402 upgrade) Chromatography Data System (Computer) have been employed. The GC is well-featured with a very large column oven, dual injection ports, dual thermal conductivity detectors (TCD's), a single flame ionization detector (FID), dual carrier gas flow controllers, and external events control. The Computer incorporates GC control, data logging, powerful peak processing, 128 K random access memory, two floppy disk drives and a printer/plotter all into one machine. The Computer can simultaneously control two GC's, each with both a TCD and FID operating. Conveniently, the
printer/plotter can plot chromatograms from both these detectors side—by—side. The controlling methods are easily built using menu—driven software. As well, the raw data transmitted from the GC may be stored to diskettes, in the event that recalculation is required at a later date.

Using many of the features listed above for the GC and Computer, a complex gas chromatography system has been designed; it employs an arrangement of columns, a column switching valve and both the TCD's and FID. Several J&W Megabore columns (0.53 mm ID) have been utilized; these fused silica capillary columns provide a quicker analysis time with better resolution than the traditional packed metal columns. A photo of the column oven interior is seen in Figure 4.8. Columns 1,2 and 3 are located on the left and Columns 4 and 5 on the right. The switching valve is mounted on the right oven wall. This same equipment is shown in schematic form in Figure 4.9. The Fischer pyrolysis reactor module is mounted atop the Side A injection block. On the column side of the injection port, a Megabore direct vaporization injection liner (84.5 mm length) is contained within a specially designed fitting. This liner has been specially designed by J&W to minimize high molecular weight discrimination, a common problem associated with heavy hydrocarbon analysis. Column 1, which is directly connected into the Side A injection liner, is a 1 m piece of uncoated (i.e. no separating phase) fused silica tubing. Known as a pre—column, it is in place to trap nonvolatiles before they travel further into the columns and foul the analysis columns. A Megabore union connects the pre—column to Column 2. This is a DB—1 Wall—Coated—Open—Tubular (WCOT) column of 30 m length and 1.5 μm phase thickness; it is capable of separating C₅ to C₄₀ hydrocarbons, over a temperature range of ambient to 320°C. The column cannot be operated above 320°C without
Figure 4.8: Gas Chromatograph Column Oven
INJECTION PORTS

A
B

COLUMN 5

COLUMN 1

COLUMN 2

COLUMN 4

COLUMN 3

DETECTORS

FID A

TCDA

TCDB

VALVE

AUXILIARY CARRIER GAS

Figure 4.9: Gas Chromatograph Column Configuration
degradation of the separating phase. Its outlet is connected to Port 1 of a four-port Valco switching valve (Model #AC4WT). To prevent condensation due to cold spots in the flow pattern, the valve has been installed in the column oven with the actuating shaft extending through the side wall and into the pneumatics compartment of the GC. This valve is automatically actuated by an air switch, which, in turn, is activated by GC external events relay #3. Medical grade air was piped into the air switch. In the off position, the flow from Port 1 passes to Port 2. A 30 m long GSQ gas–solid (micro–packed) column (Column 3) is connected to this port. The outlet of this column is connected to the Side B TCD, using a specially designed Megabore fitting. This novel column has recently been designed for the analysis of light hydrocarbons, among other applications. It is a superior replacement for packed columns such as the Porapak–Q (and related Porapaks), the Chromosorb 100 series and the Hayesep series. However, like these columns, it degrades readily at very high temperatures. This column should not be exposed to temperatures greater than 250°C. Thus, the entire column oven can be programmed no higher than 250°C. As a result, the upper range of analysis in Column 2 is significantly reduced, from C_{40} to approximately C_{24}.

An auxiliary helium carrier gas line is connected to Port 3 of the valve. The flow in this line is regulated by an added third flow controller (Porter flow controller; Varian). When the valve is in the off position, the flow from this port proceeds to Port 4. Column 4 is connected to Port 4; it is a DB–1 column of 11 m approximate length (originally 15 m) and 1.5μm phase thickness. Thus, it is just a shorter version of Column 2. The purpose of Column 4 is to restrict the flow of carrier gas between the valve and the Side A FID, to which its outlet is attached. The reason for this will be noted shortly. As the carrier gas flow that passes
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through the FID is less than the design value of 30 mL/min, make-up helium is supplied to the detector through the hydrogen line.

Column 5 is independent of all others. Its purpose is to act as a reference column for the TCD. The inlet of this DB-1 column of 30 m length, but 5μm phase thickness, is connected into the Side B injection liner. This column is also designed for the analysis of volatiles; however, it is not as proficient at separating light hydrocarbon gases as the GSQ. The outlet of Column 5 is connected to the Side A TCD.

 Normally the valve is positioned in the off position, with the shaft rotated fully counter-clockwise. When the valve is switched fully clockwise, however, it is the on mode. As a result the flow from Port 1 will now go to Port 4, and the Port 3 flow will proceed to Port 2. Thus, before the valve is switched, the pyrolysis products are routed through Columns 1 and 2, the valve, Column 3, and, finally, the TCD. Once the light hydrocarbons (C₄⁻) have passed through the valve, it is switched to the on position. Now the heavier hydrocarbons (C₅⁺) pass from Column 2 through to Column 4 and on to the FID. Column 3 is meanwhile slowly eluting the volatile gases using the auxiliary carrier gas flow. Column 4 (restrictor) was installed to prevent the FID flame from extinguishing every time the valve was switched.

Although Megabore columns are far more useful, in this case, than packed columns, they are not as resilient. As fused silica is quite delicate, the columns must be handled with utmost care. The Megabore conversion kit booklet should be consulted. As well, the GSQ column, in particular, can be easily destroyed if large
quantities of oxygen or water enter the system. For this reason, the GC carrier gas filters were replaced by three new filters: combination water/hydrocarbon, bulk oxygen and indicating oxygen. As well, ultra—high—purity helium was employed as the carrier gas.

4.1.2 Pyrolyser Temperature—Time Profile Establishment

Clearly, the final temperature attained by the pyrolyser and the time required for heat—up [Temperature Rise Time (TRT)] are of primary importance to the present work. Due to the fact that previous researchers have expressed doubts that commercial pyrolysers perform as specified, it was deemed necessary to measure the temperature—time profile of the inductively—heated ferromagnetic wires to: (1) confirm whether the temperatures attained by the ferromagnetic wires agree with Fischer's quoted Curie points; and (2) check if Fischer's claim of heating to temperature within 20–30 ms (Fischer, 1987) is valid.

As it would be impossible to attach a thermocouple and carry the leads out of the micro—reactor, a set—up similar to that employed in conventional Curie point pyrolysis operation was implemented. The ferromagnetic wire is simply suspended in the center of the coil. Provided the thermocouple measures the wire temperature at a location which corresponds to where the micro—reactor is located within the induction coil, the results will apply to the micro—reactor configuration. The micro—reactor glass is not likely to cause major variations to the manner in which the wire is heated.
4.1.2.1 Thermocouple Construction

The temperature—time profile of the ferromagnetic wires was measured by a system based on the attachment of low mass thermocouples. This approach has previously been employed by Levy and Fanter (1969) and Rastogi (1987). Very small diameter Type K (chromel–alumel) thermocouple leads (25 μm diameter) were twisted and then spot welded onto a full—length ferromagnetic wire, as recommended by Michels (1951). A strain gauge welder (AlTech Model W1200) was employed for this purpose. The very delicate 25 μm thermocouple leads were employed as a very fast response was required. The time constant of a thermocouple made with bare, butt welded 25 μm wire is quoted as 3 ms (Omega, 1985). It is likely that the response time of the thermocouples constructed in this work would be slightly longer, as the junction was almost bead—like. The weld was placed on the wire such that the thermocouple hot junction was located in the centre of the pyrolysis hot zone. To ensure that a good weld had been accomplished, it was examined under 35x magnification.

The very small diameter of the thermocouple wires made it practically impossible for the wires to fuse together at the junction when spot—welded. However, providing that the two thermocouple leads lie very close together on the ferromagnetic wire, as seen under magnification, a valid thermocouple hot junction does exist. The justification for this claim comes from Baker et al. (1963); "In a hot junction where a section of a metallic conducting medium (ferromagnetic wire) often separates the two thermocouple metals, one can consider the conducting metal to be a short length of wire composed of a third metal. If this portion of the circuit is at the same, uniform temperature, the effect will be the same as though the two metals
were joined directly at the point of entry into the uniform temperature region. This point will be the effective junction. However, it is necessary that the inhomogeneous portion be made as small as feasible."

4.1.2.2 Thermocouple Circuit

Provided a good thermocouple was attached, the ferromagnetic wire was then inserted through a holding assembling (see Figure 4.10) and secured at the top in a septum. To ensure that the thermocouple leads did not short contact through both contacting the conducting ferromagnetic wire, the upper lead was glued (Aron Alpha CE-481 Rapid Bonding Adhesive — Methyl Fast #101) to a 5 cm long piece of 1/8" OD borosilicate glass and the bottom lead was tacked to the outside of a short pyrex glass tube (1.8 mm OD) which itself was tacked with glue onto the bottom of the ferromagnetic wire. The entire assembly was then inserted in the induction coil, which was maintained at an elevated temperature. Actual thermocouple measurements (Atkins Technical Inc. Type K Digital Thermometer; Model #49700—K—C) indicated that the 300°C set point actually corresponds to a heater base temperature of 270°C. The leads were then connected to a terminal block, held at room temperature. Copper leads left the terminal block.

The output from the thermocouple was shunted through a 4.7 μF capacitor to filter out the high frequency signal originating from the induction coil. A differential DC amplifier (Ectron Corporation Model 687), employing a gain of 10, followed next in the thermocouple circuit. The output was then fed to a digital storage oscilloscope (Kikusui Electronics Corp. Model DSS 6520). This oscilloscope was externally triggered by the Curie point pyrolyser control unit. The
Figure 4.10: Temperature Measurement Apparatus
temperature–time oscilloscope traces were then photographed with a Polaroid camera (Tektronix C–5B Oscilloscope Camera).

All the electronics past the terminal block were tested for signal distortion and attenuation. A signal generator (Wavetek Model 164) fed a square wave signal of 20 Hz (corresponding to 30 ms – minimum anticipated pyrolyser response time) to the circuit. The 4.7 μF capacitor shunt did not attenuate and only very slightly distorted the input square wave. As well, the differential DC amplifier, at a gain of 10, was confirmed to neither attenuate nor distort the signal.

4.1.2.3 Troubleshooting

The above circuitry provided very good photographs depicting the heating of ferromagnetic wires to their Curie points. However, closer analysis indicated that, in all cases, the temperature which corresponded to the total thermoelectric voltage was much less than that quoted as the Curie point of the wires. For some of the ferromagnetic wires, four separate wire/thermocouple sets were tested; all yielded identical results.

It was initially believed that the ferromagnetic wire composition might be off–specification, thus yielding a different Curie point than labeled. However, the wire compositions, when plotted on a Curie point ternary diagram for nickel–iron–cobalt alloys (Bozorth, 1951), indicated similar Curie point temperatures as those quoted by Fischer. As well, the Curie point temperatures of the wires were confirmed by the application of melting point standards (Omega). Problems in the circuitry downstream of the terminal block were ruled out. Thus,
the thermocouple hot junction was suspected.

Incorrect positioning of the thermocouple within the coil was checked. When the thermocouple was located anywhere within the hot zone, however, the same end voltage resulted. Placing the thermocouple leads along the isotherm, as suggested by Jakob (1957), also caused no variation in the voltage. This is likely due to the fact that conduction losses from such a small junction are negligible. Next, various welding energies were employed (5 to 20 Joules); once again, no variation in the thermoelectric voltage was indicated. Finally, a thermocouple was placed in the high frequency (hf) coil without the ferromagnetic wire to check if the presence of the induction field caused more than just noise in the thermocouple readings. No voltage shifts were noted, indicating that the thermocouple was not ferromagnetic, and thus was not heated by the hf field. This was also observed by Rastogi (1987) and Levy and Fanter (1969). After all these checks, it was obvious that the source of the troubles was the fineness of the wires and the likelihood of variation from the calibration curve when using them at elevated temperatures.

4.1.2.4 Thermocouple Calibration

In response to the above conclusions, the 600 and 850°C thermocouple circuits were calibrated in a muffle furnace (Lindberg Laboratory Box Furnace Model 51828); a high temperature salt calibration bath was not available. The micro—thermocouple signal was compared against that of the furnace—mounted Type K thermocouple. Both were connected with Type K thermocouple extension wire into the Atkins Type K digital thermometer. As well, the micro—thermocouple amplified voltage was measured on a Fluke 8060A True RMS Multimeter.
ensure that the furnace was isothermal, measurements were performed once the furnace had reached the 900°C set point and was slowly cooling down. It was found that below approximately 500°C, the micro-thermocouple signal did not vary from the furnace-mounted thermocouple. This is reasonable as Omega (1985) quotes that slightly larger (125 μm diameter), and hence more durable, Type K bare wire thermocouples are accurate, on a long-term basis, at temperatures below 590°C. A variation between the micro- and regular thermocouple was, however, noted between 500°C and the highest temperature tested (900°C). The deviation increased in a linear fashion with temperature; the micro-thermocouple always read lower. At 900°C, an approximately 30°C difference was detected. This is in agreement with the findings of Bautista, Russel and Saville (1986) who discovered that 50 μm Type K thermocouples, formed in a manner similar to that of this work, deviated from melting point standards by up to 35°C at elevated temperatures of 450 to 950°C. The 600°C and 850°C thermocouple circuits responded slightly differently, likely due to varying wire composition. The higher temperature Curie point circuit was found to deviate less from the published calibration data than did the comparable lower temperature circuit.

4.1.3 Gas Chromatograph Operation Optimization and Calibration

A fairly complex gas chromatography system has been designed to permit analysis of the wide spectrum of pyrolysis products. However, considerable effort has also been invested in the optimization of the system operation and subsequent calibration, to ensure that accurate quantitative analyses would be obtained. The products expected from n-hexadecane pyrolysis must all be readily detected and resolvable. As well, the analyses should be performed as quickly as possible,
without sacrificing accuracy, so as to maximize efficiency.

4.1.3.1 Operation Scheme

It is obvious that when planning the operation of a gas chromatograph system, there are a number of operating variables that must be optimized in order to achieve a good analysis. A discussion detailing how the many variables were set in the current study appears in Appendix A (Section A.1). Table 4.1 summarizes the operating conditions finally chosen.

Operation in accordance with the above conditions has provided a detailed n—hexadecane pyrolysis product analysis. Specifically, resolution of the "difficult to separate" C_4— products (hydrogen to 1,3—butadiene), major C_5+ products (1—olefins, simple aromatics and polyaromatics), and n—hexadecane has been achieved. In particular, hydrogen/methane, ethylene/acetylene/ethane, propylene/propane and 1—butene/1,3—butadiene separations are possible. As well, a highly sensitive system has been achieved. The thermal conductivity detector is capable of detecting trace components of above 15 ng, whereas the flame ionization detector can identify hydrocarbons present in quantities as low as 1 ng. Furthermore, a low noise system has been achieved by operating the thermal conductivity detector at a low filament current. The careful selection of a low—bleed septum has been instrumental in decreasing the contaminant levels in the FID. Finally, two—stage carrier gas flow has resulted in adequate quenching of the pyrolysis products, good peak resolution and relatively quick analysis times.

The major downfall of the gas chromatography system is poor hydrogen
Table 4.1: Gas Chromatograph Analysis Conditions

<table>
<thead>
<tr>
<th>Carrier gas:</th>
<th>Helium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flows (mL/min)</td>
<td>A – 14; B – 10; Aux. – 10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature program:</th>
<th>33° C – 3 min.; 8° C/min.; 250° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total analysis time</td>
<td>30.12 min</td>
</tr>
</tbody>
</table>

| Valve switch: | 1.60 min |

| System temperatures (°C): | 
|---------------------------|---------------------|
| Injection port            | 325                 |
| TCD oven                  | 270                 |
| TCD filament              | 310                 |
| Ionization oven           | 350                 |

| TCD Detector: | 
|---------------|---------------------|
| Range         | 0.05 mV full–scale |
| Attenuation   | 32                  |
| Current       | 177 mA              |

| FID Detector: | 
|---------------|---------------------|
| Range         | \(10^{-10}/10^{-11}\) amp/mV |
| Attenuation   | 32                  |
| Flows (mL/min): | Air – 300; Hydrogen – 25 |
| Make–up helium | – 16               |

| Cylinder pressures (psig): | 
|---------------------------|-------------|
| Helium                    | 80          |
| Air                       | 60          |
| Hydrogen                  | 40          |
| Medical Air               | 50          |

Note: Flows were measured at 25° C and 0.88 atm.
detection. This problem has often plagued other pyrolysis researchers. Quantification of the hydrogen peak has been complicated by two factors:

1. Hydrogen and helium possess thermal conductivities which are very similar. Thus when present in small quantities, hydrogen is very difficult to detect. Alternate carrier gases, such as nitrogen or argon, could not be employed, however, as their thermal conductivity is very near that of light hydrocarbons. As a result, the situation was unresolvable, discounting elaborate solutions such as the expensive Carle Instruments, Inc. Hydrogen Transfer System.

2. The presence, if any, of air (nitrogen/oxygen) resulted in obscuration of the hydrogen peak. Lower initial column oven temperatures could have allowed for separation of the hydrogen/air. However, as noted in Section A.1, this type of operation could not be employed.

Nevertheless, the chromatography system is very powerful, and is, for the most part, very capable of accurately analyzing the complex products of n–hexadecane pyrolysis.

4.1.3.2 Calibration

As a quantitative analysis of the pyrolysis products is desired, the detector responses must be calibrated. One cannot assume that area% results will necessarily correspond to weight%, especially for thermal conductivity detectors. Rather, mass response factors must be determined for each component expected. The calibration of \( C_4 \)– components eluting from a TCD has been common practice. However, as the FID responds very similarly to most \( C_5^+ \) components, it has been suggested that calibration is superfluous (Dietz, 1967). This approximation is no
longer justified; to obtain an accurate pyrolysis product distribution, it is necessary to completely calibrate the gas chromatograph system.

A detailed calibration of the gas chromatograph system was conducted, the details of which are found in Section A.2. Several hydrocarbon mixtures, encompassing paraffins through polycyclic aromatics were prepared and employed. Samples were not available for all the hydrocarbons expected in the pyrolysis products, especially those routed to the FID. However, an accurate correlation for the FID response of a number of typical pyrolysis products has been published (Dierickx et al., 1986; Correlation X). This correlation was successfully employed to calibrate components which were not actually tested. Thus, in the end, mass response factors were available for the entire pyrolysis products spectrum. As expected, the TCD mass response factors varied extensively from unity (relative to ethylene), depending on the component. The FID factors (relative to n–hexadecane), on the other hand, were near unity for all but the aromatics. These components possessed factors of approximately 0.90. Thus, it is obvious that when mass response factors are not applied to the analysis of C_{5+} pyrolysis fraction, an overestimation of the aromatics content results.

To obtain an overall product distribution (C_4− and C_{5+} combined), a procedure similar to that proposed by Dierickx et al. (1986) was employed. Specifically, the TCD areas, relative to ethylene, were converted to an equivalent n–hexadecane area by employing two factors. The first factor converted the total TCD ethylene equivalent area to a comparable ethylene FID area. The second factor then converted the FID ethylene area to a FID n–hexadecane equivalent area. Thus, the peak areas for each product were expressed equivalent to n–hexadecane.
As all the components were expressed on an equal weight basis, the product distribution, in terms of weight%, could then be determined. As well, the areas could all be summed, to give a total representing the n-hexadecane area that would have been measured, had it not reacted. Application of the n-hexadecane area/actual weight ratio enabled translation of the total area into micrograms. Providing the factors are all accurate, the material balance closure should be 100±10%.

4.2 PYROLYSIS PROCEDURE

Rigid practices were followed for the n-hexadecane pyrolysis experiments. Specific attention was paid to ensure that the entire pyrolyser/gas chromatograph system was contaminant-free. As well, flows were continually monitored to ensure that no leaks existed in the system. During the course of the runs, a consistent daily procedure was employed, the details of which are found in Appendix A (Section A.4). A brief summary will be given here.

After heating and stabilization of the pyrolyser heater and gas chromatograph (GC) to the conditions given in Table 4.1, the system was subjected to two blank runs, first without, then with, the pyrolysis chamber inserted. The latter run was employed to store a blank baseline for the thermal conductivity detector (TCD). This profile was then subtracted during the pyrolysis runs to allow smoothing of the flow disturbances in the baseline. The two blank runs were also intended to permit elution of any contaminants that might be present; normally these were high-boiling and eluted through the flame ionization detector (FID). As well, the runs were employed to check for the possibility of any leaks throughout the
system or possible air infusion accompanying the hammer drop. Only after the system had been fully cleared and checked, was the first pyrolysis run conducted.

The following brief procedure was followed for each pyrolysis run. The micro-reactor was placed in the bottom of the pyrolysis chamber and the chamber mounted onto the pyrolyser tee. The GC switching valve was then turned on, to provide auxiliary carrier gas to the oxygen-sensitive TCD as the main carrier gas flow was then diverted to the pyrolysis chamber. Provided that no leaks were detected in the pyrolysis chamber/hammer seals, the entire assembly was then mounted through the pyrolysis reactor module so that the chamber needle passed through the injection port septum and into the GC. If the GC pressure then stabilized at the correct value (i.e. no leaks or plugs), the switching valve was turned off in preparation for a run. Just before the pyrolysis was initiated, a final pressure/flow check was performed. The gas chromatograph controlling method was then activated from the Varian 401 computer (Computer) and, providing the flow had sufficiently stabilized so that noise levels were low, the preparations continued. At this time, the delay timers were set on the timer control unit (timer A – pyrolysis time; timer B – hammer delay); as well, the pyrolysis time was set on the Fischer pyrolyser control unit. The timer control unit start was then triggered which sequentially activated the Fischer unit, whereby pyrolysis took place. At the end of the pre-set reaction time, the solenoid-activated hammer dropped to break open the micro-reactor and the quenched products were swept into the first gas chromatograph column for analysis.

After the analysis was complete, the pyrolysis chamber assembly was removed from the reactor module and the carrier gas switched back to the GC. At
this time, the micro-reactor was checked to ensure sufficient breakage. For an ideal operation, total crushing of the glass is desired. However, if less than half of the capillary glass was still intact and both the top and bottom were broken, the gases were still able to readily escape and thus adequate quenching would have occurred. After the micro-reactor wires were checked, under magnification, for coke deposition, they were discarded.
CHAPTER 5 – RESULTS AND DISCUSSION

A novel micro–reaction system coupled to a sophisticated gas chromatograph has been employed to pyrolyse n–hexadecane under conditions typical of industrial operation and, in particular, the Ultrapyrolysis process. This particular compound was chosen as it is representative of a typical gas oil. As well, n–hexadecane pyrolysis has been sufficiently studied in the past, thus enabling comparison of the results obtained herein.

In this chapter, experimental results obtained over the course of this study will be presented. The study of pyrolysis kinetics requires an accurate knowledge of the reaction temperature–time profile. Hence, Section 5.1 covers the experiments and computer simulation which were conducted in order to ascertain these reaction conditions. The successes and problems associated with construction of the n–hexadecane micro–reactors are discussed in Section 5.2. Finally, the results of the n–hexadecane pyrolyses are described and discussed in Section 5.3. A comparison of the experimental results to literature values is presented in this section, along with a proposed reaction scheme for n–hexadecane pyrolysis.

5.1 REACTION TEMPERATURE–TIME PROFILES

Throughout this study, the importance of utilizing a reaction system capable of heating rapidly to a pre–defined and constant temperature, followed by rapid cooling (quenching) has been emphasized. The micro–reaction system employed herein has been designed with the intentions of fulfilling these criteria. A number of
experiments have been conducted to confirm the actual temperature–time profile of
the reaction system. In particular, micro–thermocouple circuits were employed to
characterize the temperature–time profiles associated with both heating and
quenching of the ferromagnetic wire. As well, a simulation was conducted to
establish whether the micro–reactor cross–section, and hence the sample, heats in
such a manner that the temperature throughout is equal to that of the wire surface.

5.1.1 Temperature–Time Profile Measurement

The pyrolysis temperature attained in this reaction system depends on the
Curie point of the ferromagnetic wire employed. Hence, ferromagnetic wires with
specified Curie points of 600, 750 and 850°C were chosen for the pyrolysis
experiments. Micro–thermocouples (Type K; 25 μm diameter) were spot–welded
onto the ferromagnetic wires (Fischer; 0.4 mm diameter) corresponding to each of
the Curie points and these were, in turn, inserted in the high frequency induction
coil. The pyrolyser was then activated and traces of the actual temperature time
profiles upon heating and cooling were obtained. Throughout these experiments,
the resistance heater temperature was set at 300°C. As mentioned in Section
4.1.2.2, this setting actually corresponded to a temperature of only 270°C within the
pyrolysis zone.

5.1.1.1 Temperature–Rise–Time Determination

The temperature–time profile photographs for heating of the 600, 750 and
850°C ferromagnetic wires appear in Figures 5.1, 5.2 and 5.4, respectively. As Levy
and Fanter (1969) and Bühler and Simon (1970) indicated, the wires heat to
Figure 5.1: Temperature-Time Profile

600°C Curie Point Wire

Actual Temperature = 576°C
Temperature-Rise-Time = 52 ms
Pyrolysis Time = 100 ms

Scale: x - 20 ms/div; y - 100 mV/div (K=10)
Figure 5.2: Temperature-Time Profile

750°C Curie Point Wire

Actual Temperature = 750°C
Temperature-Rise-Time = 77 ms
Pyrolysis Time = 100 ms

Scale: x - 20 ms/div; y - 100 mV/div (K=10)
Figure 5.3: Temperature-Time Profile
750°C Gold-plated Curie Point Wire

Actual Temperature = 750°C
Temperature-Rise-Time = 77 ms
Pyrolysis Time = 100 ms

Scale: x - 20 ms/div; y - 100 mV/div (K=10)
Figure 5.4: Temperature-Time Profile

850°C Curie Point Wire

Actual Temperature = 842°C
Temperature-Rise-Time = 91 ms
Pyrolysis Time = 100 ms

Scale: x - 20 ms/div; y - 100 mV/div (K=10)
temperature in a near first-order manner. The temperature-time profiles were all generated at least twice and reproducibility was confirmed. The periodic noise exhibited on the photographs is attributed to the resistance heater.

The temperature-rise-time (TRT) was taken at that point where the positive slope fell to near zero. The TRT's obtained for the 600, 750 and 850°C wires were 52, 77 and 91 ms, respectively. These values are accurate to within ± 2 ms. Moreover, they compare fairly well to TRT's of 42 to 90 ms (Curie point temperatures – 600 to 800°C) obtained by Venema and Veurink (1985) using a Fischer 0316 pyrolyser.

A gold-plated 750°C ferromagnetic wire was also tested to determine whether the gold-plating had any effect on the heating characteristics. As seen in Figure 5.3, the heating profile is in perfect agreement with that of the un-plated wire; both TRT's were 77 ms. This is to be expected as the skin depth of the induced current, when the wire is gold-plated, is in the order of 0.2 mm at 750°C; this far exceeds the 64 nm gold plate thickness. Hence, the surface gold plating does not alter the thermal characteristics of the ferromagnetic wire.

The TRT's measured in these experiments are far in excess of the 20–30 ms TRT quoted by Fischer (1987) for a pure iron ferromagnetic wire (Curie point = 770°C). Consequently, a micro-thermocouple was attached to a pure iron wire and the heating profile of the wire, upon activation of the high frequency induction coil, was monitored. Surprisingly enough, the TRT for the pure iron wire was a lengthy 113 ms! It was then that it was discovered that Fischer was not, in fact, quoting results of their own pyrolyser. Rather, they were, without acknowledgement,
referring to the successful results attained by Bühler and Simon (1970) using a pyrolyser that the Fischer unit is supposedly modeled after. However, it is apparent that the Fischer unit coupled with the 0.4 mm diameter ferromagnetic wires do not produce the same results as the original Bühler and Simon pyrolyser which employed 0.5 mm diameter ferromagnetic wires.

Fischer (Hans-Joachim Wallstav; January 26, 1988; private telephone communication) confirmed that the Fischer 0316 Curie Point Pyrolyser, such as is employed herein, operates at the same conditions as the Bühler and Simon unit (480 kHz oscillator frequency; 1.5 kW maximum impulse wattage; and 1170 Oe magnetic field intensity). However, the Fischer 'Curie Point Pyrolyser Model 0316 Installation and Operating Instructions' quotes two stage power (4 kW impulse followed by 1 kW sustaining power). It is unlikely that the Fischer unit does, in fact, employ a larger power input as shorter TRT's than that obtained by Bühler and Simon would have been attained, providing the other operating conditions are similar. The fact that different diameter ferromagnetic wires were employed in each of the units is a further indication that the two units do not operate in the same manner. Bühler and Simon (1970) extensively described the effect of variable diameter ferromagnetic wires on the TRT's and found that for a 480 kHz, 1170 Oe pyrolyser, a 0.5 mm diameter wire was optimal. Smaller diameter wires, such as that employed in the Fischer unit, resulted in lengthened TRT's!

In these experiments, the 750 and 850°C wires exhibited shorter TRT's than that of the pure iron wire (770°C). This fact proves how dramatically the composition of the ferromagnetic wire alloy affects the time response. Although the compositions of the 750 and 850°C wires were not available, it is likely that they
possess a high cobalt content and low nickel content such that relatively fast TRT's are obtained.

5.1.1.2 Temperature Determination

From the temperature–time profiles photographs of Figures 5.1 through 5.4, the actual equilibrium temperature attained can be determined. The equilibrium voltage, accurate to within ± 4 mV, was divided by a gain of ten and then added onto the thermoelectric voltage corresponding to the 270°C heater temperature. This total thermoelectric voltage was then converted to a temperature using the 850°C calibration curve obtained experimentally. (Due to equipment problems, parts of the 600°C calibration run were deemed unusable.) As noted on Figures 5.1 through 5.4, the actual temperatures measured were 576, 750 and 842°C compared to specifications of 600, 750 and 850°C. Both the un–plated and gold–plated 750°C ferromagnetic wires reached a temperature of 750°C. The pure iron ferromagnetic wire stabilized at 769°C, which is in almost perfect agreement with the specified value of 770°C. Fischer (Hans–Joachim Wallstav; January 26, 1988; private telephone communication) stated that the nominal temperature of all of the ferromagnetic wires should be within ± 1% of the actual. With the exception of the 600°C wire, this is, in fact, true. Hence, it appears that the ferromagnetic wires have been manufactured under consistently tight specifications.

5.1.1.3 Cooling Profile

Although short TRT's and reproducible pyrolysis temperatures may be easily obtained, the decrease in temperature after shutting off the input power to the high
frequency induction coil is slow in comparison to the initial TRT. This can be seen in Figure 5.5; the time required for the 850°C ferromagnetic wire temperature to decrease from 842°C to 270°C was greater than 9 seconds. The introduction of a helium flow (approximately 14 mL/min) reduced this time significantly, to approximately 4 seconds. It should be noted that the temperature recorded is that of the wire and not the reaction products. The reaction products would, in fact, be quenched much faster than the wire since direct mixing with the helium flow should result in cooling rates in excess of $10^6$ K/s (Sundstrom and DeMichiell, 1971). As well, the pyrolysis products would be swept out of the pyrolysis hot zone in under 75 ms.

5.1.2 Dynamic Thermal Response of the Micro—reactor

Wampler and Levy (1987) and Walker (1972) have indicated that when small samples of 5 — 50 μg were coated onto the ferromagnetic wire surface, the entire sample reached the same temperature as the hot wire. In fact, for samples of less than 15 μg (Wolf, Levy and Fanter, 1974), the temperature—time profile of the sample was equivalent to that of the uncoated wire. Consequently, 15 μg was chosen as the sample size in the current study.

Unfortunately, these studies corresponded to samples that were fairly nonvolatile; hence, the bulk of the sample remained affixed to the wire throughout the pyrolysis, with only the products flashing away. As n—hexadecane is pyrolysed in the vapor phase in the current study, it was deemed necessary to investigate the dynamic thermal réponse of the micro—reactor cross—section to determine if any thermal gradients existed in the gas phase and whether the n—hexadecane does, in
Figure 5.5: Temperature-Time Profile With and Without Quench
850°C Curie Point Wire
Pyrolysis Time = 150 ms

Scale: x - 1000 ms/div; y - 100 mV/div (K=10)
Top Curve: no helium; Bottom Curve: 14 mL/min. helium
fact, reach the same temperature as the ferromagnetic wire surface.

As it was not possible to conduct thermocouple experiments with n–hexadecane in place, a computer simulation was written to model the thermal response of the micro–reactor upon heating of the ferromagnetic wire surface. To simplify matters, the n–hexadecane was assumed to be inert and heat transfer within the micro–reactor was assumed to occur through conduction only. This represents the worst–case scenario as the heat transfer is likely to be enhanced by convective and, in particular, radiative effects. The configuration of a typical n–hexadecane micro–reactor was shown in Figure 4.5. A 0.15 mm gap between the 12 mm long ferromagnetic wire and the inner surface of the Pyrex capillary provided a gas volume of $3.11 \cdot 10^{-9}$ m$^3$. The glass was sealed as close to the ends of the wire, as possible, to ensure that end effects in the micro–reactor were minimal. The heat generated at the wire surface was assumed to pass through the n–hexadecane vapor by conduction. Heat loss through the micro–reactor wall to the external helium flow was confirmed to be due to natural convention only. The heat transfer profile for heating of the micro–reactor from a constant heater temperature of 275°C (maximum setting of 311°C) to 842°C was simulated.

The differential equation of heat conduction for a cylindrical body with variable thermal conductivity is given by (Croft and Lilley, 1977):

$$\frac{\partial T}{\partial t} = a \left[ \frac{\partial^2 T}{\partial r^2} + \frac{1}{k} \frac{\partial k}{\partial T} \left( \frac{\partial T}{\partial r} \right)^2 + \frac{1}{r} \frac{\partial T}{\partial r} \right]$$

(5.1)

where,

T: temperature
The above differential equation will have numerous solutions unless an initial condition and a set of boundary conditions are prescribed. Initially, the entire system is at the temperature maintained by the heater.

\[ T(r,0) = T_0 \]  \hspace{1cm} (5.2)

where,

- \( T_0 \): heater temperature \((548.15 \text{ K})\)

Heat transfer at the surface of the wire is described by the following equation:

\[ T(r_1,t) = T_S \mid t \geq 0 \]  \hspace{1cm} (5.3)

where,

- \( r_1 \): ferromagnetic wire radius \((0.20 \cdot 10^{-3} \text{ m})\)
- \( T_S \): wire surface temperature \((1115.15 \text{ K})\)

The outer boundary condition accounts for the heat losses through the micro-reactor wall to the helium gas stream.

\[ -k \frac{\partial T}{\partial r} = U_2 \left[ T(r_2,t) - T_0 \right] \mid t \geq 0 \]  \hspace{1cm} (5.4)

where,

- \( U_2 \): overall heat transfer coefficient \((54.1 \text{ W/m}^2 \text{ K})\)
- \( r_2 \): inner radius of the micro-reactor glass wall \((0.35 \cdot 10^{-3} \text{ m})\)

The overall heat transfer coefficient incorporates both the outside convective film resistance and the conductive resistance associated with the micro-reactor glass wall.
\[
U_2 = \frac{1}{\frac{r_2}{k_g} \ln \left( \frac{r_3}{r_2} \right) + \frac{r_2}{r_3 h_3}}
\]

(5.5)

where,

- \(k_g\): thermal conductivity of Pyrex glass (1.26 W/m K)
- \(r_3\): outer radius of the micro-reactor glass wall (0.435 \(\cdot\) 10\(^{-3}\) m)
- \(h_3\): outside convective film coefficient (43.6 W/m\(^2\) K)

The outside convective film coefficient was calculated using a correlation specifically for short vertical cylinders in a natural convection environment (McAdams, 1954).

In order to solve this coupled partial-differential problem, the equations were reduced to a set of ordinary differential equations by discretizing with respect to radius. This technique is often referred to as the Method of Lines. The resultant set of equations was then solved in the time domain using the Advanced Continuous Simulation Language (ACSL); Mitchell and Gauthier, Assoc., Inc. (Concord, Mass.). The program code appears in Appendix C.

The simulation model indicated that, under the worst-case scenario, the n-hexadecane vapor would reach thermal equilibrium within 12 ms. However, an approximately linear temperature gradient across the micro-reactor was predicted. The temperature right next to the inner glass wall was 57°C cooler than that of the ferromagnetic wire. However, these results apply to the case where heat is transferred through conduction only. It is anticipated that radiative heating of the glass will be considerable, given the elevated temperature of the wire and the high emissivity of Pyrex (\(\epsilon = 0.9\)). Consequently, the micro-reactor gases would be heated to the wire temperature in a rapid fashion.
5.2 MICRO–REACTOR STUDIES

The novel micro–reaction system employed in this study represents a considerable improvement over conventional reaction systems. However, this advancement in technology has been accompanied by increased operational difficulties, particularly in the area of feedstock preparation. Since the micro–reactors are restricted to a single use, the construction of tens of micro–reactors is necessary. As a very delicate procedure is employed to construct these micro–reactors and only microgram quantities of n–hexadecane are enclosed, there may be considerable variance between micro–reactors. In fact, apparent reproducibility problems were encountered during construction. Consequently, experiments were conducted to determine the repeatability of the micro–reactor construction technique.

Construction of the numerous micro–reactors was a tricky procedure, consequently some of the micro–reactors constructed were unusable. In particular, inconsistencies in the amounts of n–hexadecane coated on each wire, as indicated by the Cahn Electrobalance, was a frequent problem. Strangely enough, construction of the 750° C gold–plated wire micro–reactors was rarely plagued by this problem; weights of approximately 15 µg were consistently measured. The inconsistencies were mainly attributed to the influence of dust and fluff. In fact, small bits of fluff, which occasionally attached to the weighing boat or coated wire, were found to weigh about 30 µg. The accuracy of the balance itself was, at times, in question; repeated weights always varied by about 4 µg; the repeatability of the balance is quoted as ±1 µg.
The actual reproducibility of the micro-reactor construction technique has been tested by "pyrolysing" micro-reactors, constructed with 300°C Curie point ferromagnetic wires, for less than 10 ms. At these conditions, no reaction should, in theory, take place. Thus, the amount of n-hexadecane enclosed within a micro-reactor can be deduced. The total peak area indicated by the gas chromatograph was converted to an equivalent n-hexadecane weight using a factor derived from extensive calibration of the flame ionization detector with known amounts of n-hexadecane.

"Pyrolysis" of 300°C micro-reactors with n-hexadecane weights of 11 to 60 μg (Cahn balance) indicated that, in fact, the micro-reactors contained similar quantities of n-hexadecane. An average weight of 11.7 μg, with a standard deviation of 0.3 μg was measured. Incorporation of the n-hexadecane weights determined for the actual pyrolysis runs (576-842°C) with those determined during the 300° pyrolyses indicated similar results. For 14 micro-reactors, with Cahn n-hexadecane weights ranging from 6 to 60 μg, an average n-hexadecane weight, as deduced through chromatography, of 12.4 μg with a standard deviation of only 1.5 μg was achieved. This amount, enclosed in the 3.11 μL micro-reactor volume, corresponds to a pressure of 0.83 atm at 300°C. As the normal boiling point of n-hexadecane is 287°C, there is no doubt that n-hexadecane was in the vapor phase during "reaction".

The above survey does not include results from all the n-hexadecane pyrolysis runs. A handful of questionable micro-reactors with Cahn n-hexadecane weights ranging from 0 to 7 μg were employed due to short supply. The total n-hexadecane weights associated with these micro-reactors averaged 6.1 μg,
indicating a significant loss of n—hexadecane during the construction procedure.

With the exception of the last micro—reactors mentioned, the n—hexadecane weights enclosed in the numerous micro—reactors have been fairly consistent. The difference between the intended 15 µg and the average 12.4 µg value can be attributed to losses during the sealing process. As a very hot torch was employed, it is likely that the n—hexadecane was, in part, vaporized and subsequently escaped during evacuation.

Surprisingly enough, the 300°C "pyrolyses" indicated that minor amounts of n—hexadecane had been converted (1 — 2.5 %) prior or during the pyrolysis period. These were included in the n—hexadecane weights mentioned above. In particular, small quantities of 1—pentene through 1—pentadecene and, especially, ethylene were evident. This conversion is mainly attributed to the fact that the micro—reactors sat in the heated pyrolysis chamber (actual temperature — 275°C) for approximately 20 minutes prior to pyrolysis; hence reactions may have occurred to a very minor extent.

The importance of good micro—reactor breakage was also highlighted during the 300°C experiments. For example, when the micro—reactor glass was entirely shattered, the conversion was restricted to approximately 1%. However, if only the top, say 3mm, of the micro—reactor was broken by the hammer, the conversion was slightly higher at 2.5%. As well, the product distribution showed very definite benzene, toluene and styrene peaks, indicating significant secondary degradation, likely attributed to a poor quench.
5.3 n-HEXADECANE PYROLYSIS

In keeping with the objectives of this study, n-hexadecane has been pyrolysed at temperatures varying from 576 to 842°C and reaction times from 100 ms to 3200 ms. As well, studies have been conducted with gold-plated ferromagnetic wires to elucidate the effect of the metal wire surface, if any. An extensive presentation and discussion of the experimental results obtained appears in this section. In particular, the outcome of pyrolyses at high temperatures and short reaction times, typical of Ultrapyrolysis, will be addressed.

5.3.1 Gas Chromatography Results

A sophisticated gas chromatography system has been employed to directly analyze the complex pyrolysis product streams. In particular, a switching valve, a number of capillary columns, dual thermal conductivity detectors and a single flame ionization detector have been employed. These detectors have been extensively calibrated to ensure accurate quantification of the pyrolysis products. For the most part this advanced chromatography system has successfully analyzed the pyrolysis products. For illustrative purposes the pyrolysis chromatograms obtained from 576, 750 and 842°C pyrolyses all at 500 ms are included; these represent Figures 5.6, 5.7 and 5.8, respectively. It is not the purpose of this sub-section to discuss the particular pyrolysis products attained and their trends with increasing temperature. Therefore, only those aspects exemplified on the chromatograms which are relevant to gas chromatography will be detailed at this time.

As clearly seen in Figures 5.6 through 5.8, the pyrolysis products have been
Figure 5.6: Pyrolysis Chromatogram - 576°C; 495 ms
2.9% n-Hexadecane Conversion
Figure 5.7: Pyrolysis Chromatogram - 750°C; 499 ms
45.5% n-Hexadecane Conversion
Figure 5.8: Pyrolysis Chromatogram - 842°C; 500 ms

86.6% n-Hexadecane Conversion
well resolved by the gas chromatography system. In particular, the 1-olefins are well distanced and difficult separations such as ethylene/ethane and 1-butene/1,3-butadiene have been achieved. The valve switch was well timed, since all the C_4—products were routed to the thermal conductivity detector for analysis. The system is highly sensitive. For example, the easily detected 1-nonenone peak on Figure 5.6 represents a mere 6 ng. As well, the noise level on the thermal conductivity detector is surprisingly low, thus considerably enhancing this detector's sensitivity.

Unfortunately, the thermal conductivity detector chromatograms were plagued by other problems. In particular, a non-reproducible disturbance interfered with quantification of the propylene and propane peaks through most of the pyrolysis runs. This disturbance appeared anywhere from 6 to 10 minutes into the analysis (column temperature: 73 — 89°C). It is attributed to a flow transition, possibly caused by the flow controllers. Despite considerable effort, it could not be eliminated. Consequently, the propylene area often had to be estimated through manual means. As the disturbance totally masked the propane peak, it had to be estimated from published product distributions at similar conditions (Depeyre et al., 1985).

The other major problem associated with the thermal conductivity detector chromatogram was the obscuration of the hydrogen by an apparent "air" peak. Ordinarily hydrogen would be observed just before methane. As noted in Section 4.1.3.1, this situation is unavoidable given the current chromatography system. However, the presence of air was not anticipated as the micro-reactors were carefully evacuated during construction to ensure that no air remained. As this
situation was particularly disturbing, a Porapak Q packed metal column was temporarily installed to analyze the light gases from pyrolysis. Experiments using this column indicated that, providing the micro-reactors were evacuated for longer than 60 s and the hammer seal was tight, no air was present within the pyrolysis system. Consequently, it is thought that the "air" peak may be due to a disturbance associated with the micro-reactor breakage which would not have appeared when employing the packed column, due to a dampening effect by the packing. The fact that a significant 1-hexadecene peak was not observed is further evidence that n-hexadecane oxidation did not occur.

The final major problem encountered was the presence of contaminant peaks in the later stages of the flame ionization detector chromatogram. This problem is particularly evident in Figure 5.7. These contaminants, at times, caused obscuration of the higher 1-olefin (tetradecene and heavier) and polyaromatic peaks. The fact that the analysis was performed at such a high sensitivity meant that even slight contamination could cause significant background to the actual pyrolysis products. The contamination existed despite careful attempts to avoid contamination. In particular, the ferromagnetic wires and pyrolysis chambers were carefully cleaned before use. Clean forceps were employed at all times; fingers never touched the septa, ferromagnetic wires, micro-reactors nor pyrolysis chamber needles. Nevertheless, the contaminant peaks persisted and, in the end, were mainly attributed to slight degradation of the injection port septum, as it was maintained at a temperature slightly above the specified maximum.

In progressing from Figure 5.6 through 5.8, it is evident that increased temperatures yield increased product complexity. Consequently, identification
of the products became much more difficult. In particular, a multitude of products were detected in the C₅ to C₇ range for the 750 and 842°C runs. These products were thought to be isomerized olefins, diolefins, cyclic olefins or even cyclic diolefins, based on the results of Herrera et al. (1981). They analyzed pyrolysis gasoline, a C₅⁺ by-product of light hydrocarbon pyrolysis, using a gas chromatography–mass spectrometry system. A similar system, applied to this study, would have facilitated easier identification of the complex pyrolysis product streams.

5.3.2 Product Distributions

Although the above mentioned problems complicated the pyrolysis products analysis, they did not prevent attainment of the product distributions for the numerous pyrolysis runs conducted. In fact, as exemplified by the product distribution data in Appendix B, rather detailed product distributions were attained for all the presented runs. The accuracy of the distributions is reflected in the fact that all but three of the 17 runs had material balance closure of 95 – 105 %. Evidently, the extensive series of calibration factors employed were well–determined.

In addition to the product distribution and material balance information, the actual pyrolysis time, n–hexadecane conversion, n–hexadecane initial weight and, finally, the initial and final pressures are presented in the tables of Appendix B. The actual pyrolysis time represents the time displayed at the end of the run by the timer control unit, rather than the set value. However, through the course of the discussion, the set values will be referred to. This time, of course, includes the
temperature rise period. The pressure slightly increased during pyrolysis because the additional moles formed were restricted to a constant volume batch reactor.

As data in tabular form is difficult to interpret, a number of plots have been included to present the product distributions as a function of both time and temperature. In an effort to minimize confusion, the products have been grouped as follows: hydrogen/methane, ethylene, other gases (C$_4$—), C$_5$—C$_9$ 1-olefins, C$_{10}$—C$_{15}$ 1-olefins and, finally, aromatics. The C$_4$— fraction includes ethane, propylene, propane, butenes and 1,3-butadiene, when present. The two 1-olefin groups encompass the entire range of 1-olefins; these were detected in all the runs. The C$_5$+ diolefins, cyclic olefins and cyclic diolefins are not represented; these components make up 2 — 10 wt% of the overall product stream for conversions ranging from 50 — 90%.

Figure 5.9 demonstrates the product distributions for the 500 ms, 576, 750 and 842°C pyrolyses, the chromatograms of which were shown in Figures 5.6, 5.7 and 5.8. At 576°C there is obviously little conversion and thus the product distribution is difficult to ascertain from Figure 5.9. However, as the temperature is increased at constant reaction time, significant trends develop. At 750°C, 45.5% of the n-hexadecane was converted yielding predominantly C$_5$—C$_{15}$ 1-olefins, "other gases" and ethylene (8.8 wt%); most of these are primary products. The C$_5$—C$_9$ 1-olefins were more prevalent than the heavier 1-olefins. As well, the hydrogen/methane and aromatics fractions, although in smaller quantities, were on an upward trend. It is evident that once the conversion had reached about 45.5%, secondary reactions, such as higher olefin decomposition and the Diels—Alder mechanism, began to play a vital role. This role intensified as the reaction
Figure 5.9: Product Distribution – 500 ms Pyrolysis

- $\circ = H_2/CH_4$
- $\triangle = C_2H_4$
- $\ast = \text{other gases}$
- $\times = C_5-C_9 \text{ 1-olefins}$
- $\diamond = C_{10}-C_{15} \text{ 1-olefins}$
- $\triangledown = \text{aromatics}$

Product Yield (wt%) vs. Reaction Temperature ($^\circ$C)
temperature was increased. At 842° C, 86.6% of the n-hexadecane was converted and a significantly different product distribution was attained. The aromatics and hydrogen/methane were roughly equivalent to the total C₅—C₁₅ 1-olefin fraction. Once again the lighter 1-olefin fraction was more prevalent than the heavier. As well, the ethylene (27.6 wt%) and "other gases" yields were much higher than that attained at 750° C. Thus, it is obvious that secondary reactions dominated this high conversion run.

As the initial product distribution was not clearly shown by Figure 5.9, Figure 5.10, which shows the product distributions obtained from pyrolyses at a constant temperature of 576° C and a reaction time range of 100 to 3200 ms, has been included. Under these conditions, n-hexadecane conversions from 2.6 to 8.3 % were attained and primary products dominated. In theory, n-hexadecane conversion should be minimal when pyrolysing at 576° C for short durations (less than 500 ms). However, as clearly demonstrated in Figure 5.10, quantifiable conversion has occurred at the short reaction times. Strangely enough, the ethylene yield exceeded that of all the other fractions. As well the aromatics production was non-zero. Since similar results were achieved during the supposed non-reactive conditions of 300° C and 10 ms, it is evident that, in both cases, conversion has occurred due to the lengthy pre-heat (275° C) and stabilization period to which the micro-reactors were subjected prior to pyrolysis. Considering this fact, the trends of Figure 5.10 all seem reasonable. At these low conversions, the 1-olefins were the most predominant. In fact, the heavier 1-olefins were more prevalent until 3200 ms, indicating that these olefins did not decompose until subjected to lengthy reaction times. The ethylene yields exceeded the "other gases" over the entire temperature range, with ethylene accounting for 1.7 wt% at 3200 ms. The
Figure 5.10: Product Distribution
576°C Pyrolysis

- $\circ = H_2/CH_4$
- $\triangle = C_2H_4$
- $+ = $ other gases
- $\times = C_5-C_9$ 1-olefins
- $\diamond = C_{10}-C_{15}$ 1-olefins
- $\triangledown = $ aromatics
hydrogen/methane fraction, although on a slightly upward trend, was fairly negligible. Consequently, it appears that for conversions below 10%, primary products, such as the C₅—C₁₅ 1-olefins, ethylene, ethane, propylene and 1-butene, dominate the product distribution.

The product distributions for pyrolyses conducted at 750°C and 100 to 1100 ms are displayed in Figure 5.11. Overall these runs were the most consistent in terms of n-hexadecane weight and overall material balance. Consequently, the trends exhibited should be highly reliable. Like the 300°C and 576°C short reaction time runs, the 750°C, 100 ms pyrolysis (5.6% conversion) exhibited an ethylene yield which is high relative to the other products. At a slightly longer reaction time (250 ms; 27.4% conversion), the C₅—C₉ 1-olefins constituted the majority of the product stream with the C₁₀—C₁₅ 1-olefins, "other gases" and ethylene (5.2 wt%) less but equally prevalent. The hydrogen/methane and aromatics were also on the upswing, indicating that secondary reactions were increasing in prominence. These trends remained relatively unchanged until between 800 ms (60.7% conversion) and 1100 ms (74.5% conversion) at which time the 1-olefin yields leveled off while the "other gases" and ethylene continued to increase. By 1100 ms, the ethylene yield had reached 13.4 wt%. The aromatics yield was uncharacteristically high at 800 ms. As the micro-reactor was well broken during the quenching operation, this high yield must be attributed instead to the fact that very little n-hexadecane was present in the micro-reactor (3 µg). Consequently, surface effects may have been significant.

Finally, the product distribution for the 842°C pyrolysis runs is given in Figure 5.12. This plot is particularly important because it exhibits the product
Figure 5.11: Product Distribution
750°C Pyrolysis

- $\odot = \text{H}_2/\text{CH}_4$
- $\triangle = \text{C}_2\text{H}_4$
- $\text{+} = \text{other gases}$
- $\times = \text{C}_5-\text{C}_9\ 1$-olefins
- $\diamond = \text{C}_{10}-\text{C}_{15}\ 1$-olefins
- $\triangledown = \text{aromatics}$
Figure 5.12: Product Distribution
842°C Pyrolysis

- ○ = H₂/CH₄
- △ = C₂H₄
- + = other gases
- × = C₅–C₉ 1-olefins
- ♦ = C₁₀–C₁₅ 1-olefins
- ▼ = aromatics
distributions over a very large conversion range (100 ms - 10.6%; 800 ms - 91.8%). Consequently, the various stages of n-hexadecane pyrolysis can be deduced. At a short reaction time of 100 ms, the \( C_{10} - C_{15} \) then \( C_5 - C_9 \) 1-olefins were most prevalent. As aromatics were detected, it is obvious that the preheat period still had an effect on this run. However, the pyrolysis evidently proceeded to an extent sufficient to mask elevated ethylene yields. Nevertheless, the conversion was lower than expected; this is attributed to the fact that the temperature-rise-time for 842°C is a lengthy 91 ms. Consequently, the reaction was still in its initial stages at 100 ms.

A large increase in conversion (to 47.0%) was achieved by pyrolysing for a slightly longer duration (250 ms). As is clearly demonstrated on Figure 5.12, ethylene and the "other gases" dominated; however, the \( C_5 - C_9 \) 1-olefins were also quite prevalent. In fact, this light olefin fraction reached its maximum 842°C yield at 250 ms. The \( C_{10} - C_{15} \) 1-olefins, on the other hand, were sufficiently decomposed such that they were superseded by the hydrogen/methane fraction. The aromatics yield remained very low. However, when the pyrolysis duration was extended to 500 ms (86.6% conversion), aromatics, such as benzene, toluene and styrene, became much more prevalent. As well, the hydrogen/methane content increased along with ethylene and the "other gases". In fact, the ethylene and propylene yields reached 27.7 and 13.6 wt%, respectively.

In the 800 ms (91.8% conversion) run, the aromatics and hydrogen/methane yields far exceeded those of the 1-olefins. In fact, these streams each accounted for approximately 10 wt%. Another interesting trend developed between 500 and 800 ms. The ethylene yield leveled off, whereas the "other gases" started to decrease.
Furthermore, C_5+ diolefins, cyclic olefins and cyclic diolefins constituted approximately 11 wt% of the product stream (Table B.4). These compounds were also noted by Depeyre et al. (1985) under similar conditions. Based on these results, it is evident that at high temperatures and sufficiently long reaction times, secondary products such as hydrogen, methane, diolefins, and aromatics comprise a significant portion of the product stream, at the expense of primary products.

As the latter run was conducted at a high temperature (842°C) and exhibited a high conversion, a significant pressure increase over the course of the run was expected. The initial pressure, at conditions, for this run was calculated as 1.3 atm. The increase in moles associated with pyrolysis then caused the pressure to escalate to 8.4 atm. As the formation of paraffins was not noted, it is likely that the pressure effect was minimal and merely caused a slight increase in the aromatics yield (Section 2.4.1.5).

5.3.3 Surface Effects

Despite the findings of Jackson and Walker (1971) and Jones and Moyles (1961), there is still doubt as to whether the hot ferromagnetic wire surface is, in fact, inert. Consequently, 750°C micro-reactors were constructed with gold-plated ferromagnetic wires (64 nm gold thickness) and subsequently pyrolysed at reaction times varying from 100 to 1100 ms. Depeyre et al. (1985), in experiments with both Incoloy and quartz (inert) reactors, found that the Incoloy system produced much higher ethylene, aromatic and hydrogen yields than the quartz reactor at the same conditions. Thus, these fractions were plotted for both the gold-plated and non-plated ferromagnetic wire runs. As is seen in Figure 5.13, the ethylene,
Figure 5.13: Product Distribution
750°C Pyrolysis
Comparison With Runs Using Gold-plated Ferromagnetic Wires

- \( \text{H}_2/\text{CH}_4 \)
- \( \text{C}_2\text{H}_4 \)
- Aromatics

Gold-plated wires

- \( \text{H}_2/\text{CH}_4 \)
- \( \text{C}_2\text{H}_4 \)
- Aromatics

Non-plated wires

Product Yield (wt%) vs. Reaction Time (ms)
hydrogen/methane and aromatics yields actually agreed phenomenally well with data collected using un-plated 750°C wires, previously shown in Figure 5.11. The 1-olefin and "other gases" yields, although not displayed, were also similar. As well, examination of the micro-reactor wires post-pyrolysis revealed no coke deposition. Therefore, despite the fact that the metal surface/volume ratio of the reactor was very high (49 cm⁻¹) compared to previous n-hexadecane reactors (Table 2.1), no catalytic behaviour was detected.

5.3.4 Effect of Reaction Time and Temperature

The previous discussion has indicated how dramatically conversion increases with reaction time and, in particular, temperature. However, when conversion is plotted as a function of temperature and reaction time, as has been done in Figure 5.14, the trends become even more apparent. This figure clearly indicates that even at long reaction times (3200 ms), only very low conversions (less than 10%) can be attained when pyrolysing at low temperatures (576°C). This implies that the reaction is very slow under these conditions. However, when the pyrolysis temperature is increased to 750°C, the pyrolysis reaction speeds up considerably such that a n-hexadecane conversion of 74.5% can be attained within only 1100 ms. At 842°C, the conversion reached 86.6% in only 500 ms; the ethylene yield obtained from this run corresponded to a significant 27.7 wt%. However, the conversion leveled off when the reaction time was extended; inhibition was likely the cause. The high temperature/long residence time data of Depeyre et al. (1985) was also plagued with this problem. Thus, it is obvious that operation at ultrapyrolytic conditions of 842°C and 500 ms is optimal, as a high ethylene yield is obtained without the risk of severe inhibition.
Figure 5.14: Effect of Temperature on Conversion

![Graph showing the effect of temperature on n-Hexadecane conversion over reaction time. The graph compares conversion rates at different temperatures: 576°C, 750°C, 750°C (gold), and 842°C. The x-axis represents reaction time in milliseconds (ms), ranging from 0.0 to 3200.0, while the y-axis represents the n-Hexadecane conversion (%).]
The conversions obtained with the 750°C gold–plated ferromagnetic wires have also been plotted on Figure 5.14. With the exception of the 1100 ms run, they agree perfectly with the conversions of the non–plated wire runs, thus indicating that the metal surface had no influence on the reaction.

5.3.5 Kinetic Parameter Estimation

It is well known that paraffin pyrolysis follows approximately first order kinetics. Consequently, the reaction rate constants and activation energy for \( n \)-hexadecane pyrolysis have been determined assuming the overall decomposition is of the first order. For a first order reaction in a constant volume batch reactor, such as was employed in this study, the following equation applies:

\[
 k = \frac{1}{t_r} \ln \frac{1}{1 - x}
\]  

(2.34)

where,

- \( k \): first order reaction rate constant
- \( t_r \): reaction time
- \( x \): fractional conversion

If the expression \( \ln [1/(1-x)] \) is plotted versus time, the slope of the best–fit line corresponds to the rate constant. In this manner, the rate constants have been determined at each of the pyrolysis temperatures using the method of least squares to regress the data. Figures 5.15, 5.16 and 5.17 display the rate constant evaluation at 576, 750 and 842°C, respectively. The temperature–time profile experiments indicated that the reaction temperature is a function of time, in addition to temperature, for the first 52 – 91 ms of the pyrolysis. Consequently, the very short residence time data (100 ms) was discarded when the best–fit lines, and thus the
Figure 5.15: Rate Constant Evaluation
576°C Pyrolysis

\[ k = 0.021 \text{ s}^{-1} \]
Figure 5.16: Rate Constant Evaluation
750°C Pyrolysis

Graph showing the relationship between ln[1/(1-x)] and Reaction Time (ms) with two types of wire markers:
- ○ = non-plated ferromagnetic wire
- △ = gold-plated ferromagnetic wire

The line on the graph indicates a rate constant of k = 1.221 s⁻¹.
Figure 5.17: Rate Constant Evaluation

842°C Pyrolysis

\[
\ln \left( \frac{1}{1-x} \right) = k \times \text{Reaction Time (ms)}
\]

\[k = 5.358 \text{ s}^{-1}\]
rate constants, were determined from the data of Figures 5.15 through 5.17. As can be seen from these figures, good fits were obtained at 576 and 750° C; thus verifying that n-hexadecane pyrolysis is indeed first order. More data would have aided in the determination of the best-fit line for the 842° C runs. As it was, only two points could be used, as the 800 ms data was plagued by inhibition.

Since the reaction rate constants are now available, the half-lives of the reaction can be calculated to assess its speed at various temperatures. These values are tabulated below.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate Constant (s⁻¹)</th>
<th>Half-life (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>576</td>
<td>0.021</td>
<td>33,000</td>
</tr>
<tr>
<td>750</td>
<td>1.221</td>
<td>568</td>
</tr>
<tr>
<td>842</td>
<td>5.358</td>
<td>129</td>
</tr>
</tbody>
</table>

The fact that the half-life is so large at 576° C indicates just how slow the reaction is under these conditions. Still, the reaction is orders of magnitude slower at 275° C. In contrast, half-lives of less than 600 ms above 750° C exhibit how fast this reaction is at higher temperatures. Consequently, one can understand just why Ultrapyrolysis, which is characterized by reaction temperatures in excess of 700° C and reaction times less than 500 ms, is considered to be a fast pyrolysis process.
As mentioned above, the reaction rate constant is a function of temperature and is expressed by the well-known Arrhenius expression:

\[ k(T) = A_0 e^{-E_a/RT} \]  

(5.6)

where,

\( A_0 \): frequency factor
\( E_a \): activation energy
\( R \): universal gas constant

As reaction rate values are known at three temperatures, the activation energy, as well as the frequency factor, can be determined. A plot of the natural logarithm of the rate constant versus the inverse temperature, yields \( E_a/R \) as its slope and the natural logarithm of the frequency factor as its \( y \)-intercept. Consequently, the activation energy and frequency factor are easily determined. Figure 5.18 has been prepared in order to establish these parameters. The data of this work is perfectly linear; no leveling of the curve at low inverse temperature (high temperature) is evident. This is expected as the rate constants were determined using short reaction time data; consequently, inhibition was not expected to affect the kinetic parameter determination. A best-fit line through the data yields the following expression for the rate constant:

\[ k(T) = 3.00 \cdot 10^8 e^{-39,400/RT} \]  

(5.7)

Out of interest, this expression was used to predict n-hexadecane conversion at conditions typical of the preheat: 275°C and 20 minutes. The predicted conversion was, at 0.007%, much less than that which actually occurred. As the data which established this Arrhenius relation was at substantially different conditions, this predicted value should not be heavily relied upon. There is no doubt that 1 – 2.5% of the n-hexadecane was actually converted.
Figure 5.18: Activation Energy Evaluation

\[ \ln k \]

Inverse Temperature (1/Kx10^3)

\[ E_o/R = 19837 \text{ K} \]

\[ E_o/R = 16309 \text{ K} \]

This Work
Rastogi
The value obtained for the activation energy (39.4 kcal/mol) is significantly lower than the accepted n–hexadecane activation energy of 57 kcal/mol. However, when the propane pyrolysis kinetic data of Rastogi (1987), which was collected using the same micro–reaction system, was plotted on Figure 5.18, it was noted that the two best–fit lines almost overlapped. This is to be expected as propane pyrolysis typically exhibits an activation energy which is only slightly less that of n–hexadecane. As well, the rate constants for the propane pyrolysis were slightly lower. According to Froment (1981), this is also correct behaviour. As Rastogi employed a similar micro–reactor but much simpler analysis system, it is apparent that the low activation energy is not due to any errors associated with the complex product quantification in this study. Rather, the cause must be traced to the pyrolysis apparatus and its operation.

5.3.6 Comparison to Reported Data

In an attempt to validate the data acquired in this study, comparisons will be made to previously published data on n–hexadecane pyrolysis. The Depeyre et al. (1985) study, in which n–hexadecane was pyrolysed over a range of 600 to 850°C, is the key reference. Unfortunately, comparisons at equivalent conditions cannot be made as Depeyre et al. did not publish residence times; rather they provided incorrectly determined, and likely underestimated, space times ranging from 500 to approximately 1200 ms. However, the product yields as a function of conversion, can be compared. Figure 5.19 is such a plot; on it the 750,842°C (500–1100 ms) data of this study have been superimposed over the 600–750°C, long space time data of Depeyre et al. The higher temperature Depeyre et al. data was not plotted due to space restrictions. As seen in Figure 5.19, the trends are in
Figure 5.19: Comparison With Reported Product Distributions

- $\text{H}_2/\text{CH}_4$
- $\text{C}_2\text{H}_4$
- other gases
- $\text{C}_5-\text{C}_9$ 1-olefins
- $\text{C}_{10}-\text{C}_{15}$ 1-olefins
- aromatics

---

Product Yield (wt%)

$n$-Hexadecane Conversion (%)
general agreement. The 1-olefins are relatively prevalent between 60 to 75 % conversion, but decrease significantly at higher conversions. This decrease is accompanied, in both studies, by a dramatic increase in ethylene, "other gases", hydrogen/methane and aromatics. As well, the same downward trend of the "other gases" fraction at conversions exceeding 86% is exhibited by both studies. On the basis of these comparisons, it can be concluded that the data of this study and that of Depeyre et al. exhibit similar product trends as conversion is increased.

Given the problems associated with the Depeyre et al. data, it is necessary to, in some way, compare the data of this study to other references. Consequently, the kinetic data has been plotted against that of all the previous n–hexadecane researchers, as shown in Figure 5.20. The reported data covers a range of 500 to 850 °C and has been discussed in detail in Section 2.5.3. As seen in Figure 5.20, the low temperature data of this study (576 °C) agrees fairly well with reported data in the same temperature range. In fact, the best-fit line, if extrapolated, would intercept both the the Voge and Good (1949) and Rebick (1981) data points. As mentioned in Section 2.5, these studies are highly reliable. At higher temperatures, however, a large deviation between the data of this study and, particularly that of Depeyre et al. (1985), is noted. It is likely that this deviation would be much smaller had Depeyre et al. not: (1) erred in their space time, and hence rate constant, calculations; and (2) employed a rather hot feed preheat (480 °C) section.

Nevertheless, the data of this study does generally lie below that of previous researchers, indicating that lower rate constants and, hence, lower conversions have been attained. As well, the best-fit line is not as steeply sloped, indicating that the activation energy of this study is lower than that attained by previous researchers;
Figure 5.20: Comparison With Reported Kinetic Data

- ○ = Zhou et al.
- △ = Depeyre et al.
- + = Rebick
- × = Groenendyk et al.
- ◆ = Voge & Good
- ▼ = Panchenkov & Baranov
- ☑ = This Work
This was mentioned earlier. Also, no inhibition, as detected in the Depeyre et al. data, was noted at the highest temperature. This is due to the fact that the 842°C reaction rate constant was evaluated using short reaction time data only; consequently, inhibition was not an issue.

The above differences can be attributed to a number of factors. As stated by Fabuss et al. (1964), activation energies are often low if a reaction system is heat transfer–limited. A decrease in the activation energy as the temperature increases is also noted if insufficient heat is available for the reaction. As the data of this study did not exhibit the latter trend and as it was confirmed that the system does, in fact, reach the temperatures intended, there is no possibility of heat–transfer limitations within the micro–reaction system.

The low data obtained in this study may also be attributed to problems associated with the micro–reaction system. As only three data points have set the line on Figure 5.20, there is a significant possibility of misinterpretation. In particular, there is a large gap between 576 and 750°C in which no data was obtained. In this same region, Rastogi (1987) found that the rate constant sat above the best–fit line, indicating that the trend was perhaps upwards followed by a slight leveling off as temperatures were increased. Thus, he concluded that inhibition had, in fact, significantly affected the high–temperature pyrolysis results. Unfortunately, due to the lack of data in this study, no conclusions can be made as to whether this was in fact the case with n–hexadecane pyrolysis. However, as the data points do lie nicely on a common line, it is believed that this latter reasoning is not the cause of the low data.
The previous n–hexadecane pyrolysis researchers all employed tubular–flow reaction systems, which were often fairly sizable. The high temperature (greater than 600°C) studies (Zhou et al., 1987; Depeyre et al., 1985) likely experienced significant radial and axial thermal gradients. Consequently, the actual pyrolysis temperature was not well–defined. Furthermore, it is well known that accurate determination of the residence time in a tubular–flow reactor is difficult. Thus, all of the previous researchers chose to just quote the space time. This time, however, does not account for the increase in moles which always accompanies pyrolysis nor thermal gradients. It can, nevertheless, still be employed to predict the rate constant, provided the correct equations are employed. However, as noted previously, both Zhou et al. and Depeyre et al. erred in this regard. Obviously, it is difficult to establish the reaction conditions when a flow reactor is employed. Thus, it is likely that this is the first n–hexadecane pyrolysis study where the reaction conditions have been precisely known and controlled.

As well, past researchers did not, in many cases, recognize the importance of rapidly quenching their product streams. Rather, they employed primitive air/ice traps, if anything at all. Consequently, the reactions likely proceeded on longer than intended and higher conversions resulted. The effect of the slow quench would increase in significance as the reaction temperature increased, due to the increased speed of the reaction. Thus, their conversions would deviate more and more from those attained with a rapid quench as the temperature was increased, until inhibition finally slowed down the reaction. Consequently, the rate constants achieved would be higher than those attained in this study, as would the activation energy.
Based on the above discussion, it is apparent that poor reaction control on the part of past researchers is the most plausible cause of the discrepancy between the data of this study [and that of Rastogi (1987)] and previous researchers. It is not likely that the presence of more data would alter this finding. Finally, a word of caution; the calculation procedures of literature data should be carefully reviewed for correctness. Errors may exist, as was the case for the Zhou et al. and Depeyre et al. studies.

5.3.7 Generalized Reaction Scheme

To sum up the findings of this study, a generalized reaction scheme for n–hexadecane pyrolysis is proposed. This scheme, illustrated in Figure 5.21, incorporates both literature trends, as described in Chapter 2, and those exhibited by the experiments of this study. Briefly, the scheme proposes that, for n–hexadecane conversions below 10%, the product slate is comprised only of primary products, such as the C₂–C₁₅ 1–olefins and the C₁–C₃ paraffins. As the conversion is increased slightly, secondary reactions begin to occur. First of all, the heavier 1–olefins decompose into lighter 1–olefins. Although not noted on Figure 5.21, decomposition of the lighter 1–olefins does not proceed until the conversion exceeds roughly 70%.

At moderate conversion levels (x > 40%), C₄–C₁₃ 1–olefins typically dehydrogenate to form diolefins, such as 1,3–butadiene. The butadiene then immediately combines with available ethylene or propylene to form simple aromatics, such as benzene, toluene, ethylbenzene, styrene and the xylenes. This reaction proceeds according to the Diels–Alder mechanism; consequently, cyclo
Primary Reaction:
\[ n-C_{16}H_{34} \rightarrow C_2-C_{15} \text{ 1-olefins} \: + \: C_1-C_3 \text{ paraffins} \]
\( (x < 10\%) \)

Secondary Reactions:
\[ C_5-C_{15} \text{ 1-olefins} \rightarrow C_2-C_4 \text{ olefins} \: + \: C_1-C_3 \text{ paraffins} \]
\( (x > 10\%) \)
\[ C_4-C_{13} \text{ 1-olefins} \rightarrow C_4-C_{13} \text{ diolefins} \: + \: H_2 \]
\( (x > 40\%) \)
\[ C_2,C_3 \text{ olefins} \: + \: C_4H_6 \rightarrow \text{simple aromatics} \: + \: H_2 \]
\( (x > 40\%) \)
\[ C_3H_8 \text{ and } C_3,C_4 \text{ olefins} \rightarrow \text{CH}_4 \: + \: \text{C}_2\text{H}_4 \]
\( (x > 85\%) \)
\[ \text{simple aromatics} \: + \: C_4H_6 \rightarrow \text{polyaromatics} \: + \: H_2 \]
\( (x > 85\%) \)
olefins are formed as intermediates. Once the conversion exceeds approximately 85%, propane, propylene and the butenes typically decompose to form large quantities of ethylene and methane. Significant inhibition of the pyrolysis mechanism also occurs. Concurrently, remaining butadiene combines with the now prevalent simple aromatics to form polyaromatics through a Diels–Alder mechanism. For example, naphthalene (two–ring polyaromatic) is formed through addition of butadiene to benzene.

If the pyrolysis severity is further increased, naphthalene is likely to combine with butadiene to form three–ring polyaromatics, such as phenanthrene and anthracene. Typically this does not occur until the conversion level exceeds 99% (Depeyre et al., 1985). Consequently, these products were not detected in the current study. Nevertheless, presuming pyrolysis had continued, it is likely that high molecular weight, hydrogen–deficient, multi–ring polyaromatics would have been formed next. These compounds are, in fact, the much–dreaded coke precursors.
CHAPTER 6 – CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The vapor–phase pyrolysis of n–hexadecane has been studied with the intent of expanding the current knowledge of heavy paraffin pyrolysis, particularly at previously unreported ultrapyrolytic conditions. A novel micro–reaction system, which incorporated rapid heating to a predetermined and constant temperature, followed by rapid quenching was chosen as it was deemed the only system available that satisfied the requirements for attainment of valid kinetic data, especially within the Ultrapyrolysis regime. n–Hexadecane was selected due to the fact that it well represents a typical gas oil, and hence may also shed some light onto pyrolysis of this heavy feed. As well, there was sufficient high temperature, although long reaction time, data in the literature to allow comparison. The conclusions that can be reached from this study are as follows:

(1) The conventional flow reaction systems employed by previous n–hexadecane researchers are deemed inadequate for kinetic study due to the fact that reaction time and temperature cannot be accurately determined nor controlled.

(2) The micro–reaction system used in this study has a reaction temperature–time profile that approximates the ideal half square wave. Heating to a pre–determined and constant temperature was achieved in less than 100 milliseconds by employing a Curie point pyrolyser. After a well controlled reaction time, the pyrolysis products were quenched through
direct gas mixing, and hence the reactions were stopped within mere milliseconds. Furthermore, studies with both metal and gold–plated heating surfaces indicated no evidence of catalysis by the hot metal surface.

(3) A rather sophisticated gas chromatograph system capable of resolving the many pyrolysis products successfully analyzed the complex pyrolysis products. Excellent material balance closure was exhibited.

(4) n–Hexadecane pyrolysis has been successfully studied at reaction temperatures and times within the industrial and Ultrapyrolysis range of interest: 576 to 842 °C; 100 – 3200 ms. The reaction was very slow at 576°C with a maximum conversion of less than 8%. However, almost complete conversion was attained at 842°C within less than 500 ms. Ethylene yields of 28 wt% indicate that these ultrapyrolytic conditions are optimal.

(5) The first order kinetic data, though limited, shows a consistent trend. However, the activation energy is significantly lower than that previously reported. This has been attributed to poor reaction temperature/time control on the part of previous researchers. In particular, inadequate quenching of the reactions has been faulted. Consequently, reactions proceeded on longer than intended, thus causing higher conversions and reaction rate constants, particularly at elevated temperatures where the reactions are very fast.

6.2 RECOMMENDATIONS FOR FUTURE WORK

Hydrocarbon pyrolysis is a highly complex reaction. Consequently, there is still much to be learned. In particular, the following items should be addressed.

(1) Further experiments should be conducted with data collection at numerous
temperatures to gain more confidence in the very different kinetic trends exhibited by this micro-reaction system.

(2) More advanced analytical technology should be employed to facilitate easier identification of the numerous pyrolysis products. Gas chromatography/mass spectrometry is recommended.

(3) The study of other heavy hydrocarbons should be undertaken as there is still so much more to learn, particularly at conditions typical of Ultrapyrolysis. Initially, pure components from the olefin, naphthene and aromatic groups should be studied. Only then should mixtures and, in the end, whole oil fractions be pyrolysed.
REFERENCES


APPENDIX A
EXPERIMENTAL PROCEDURE, MATERIALS
AND CHEMICALS

A.1 GAS CHROMATOGRAPH OPERATION SCHEME DEVELOPMENT

When designing a gas chromatographic analysis, especially one as complex as that employed in this study, a number of operating parameters must be set in an optimal fashion in order to achieve a successful end result.

A.1.1 Temperature Program

The operating temperature(s) is often the first parameter which is set. In the analysis of wide hydrocarbon ranges, temperature programming is often employed; thus, five parameters exist — initial temperature, initial hold time, programming rate, final temperature and final hold time. Due to system constraints, only the programming rate and hold times were truly variable. As cryogenic cooling could not be applied, the initial column oven temperature had to be set relative to that which could be maintained through ambient-only cooling; this temperature was determined to be 33°C. In order to facilitate the best hydrogen/methane separation, this temperature was maintained for 3 minutes.

The implementation of cryogenic (liquid CO₂) cooling to achieve a low initial temperature was unsuccessful; it resulted in extensive noise to the TCD chromatogram. This noise was caused by flow disturbances generated by cycling
(on/off) of the CO\textsubscript{2} supply. As Megabore columns possess a very small diameter and are wall–coated rather than packed, they rapidly adjust to temperature fluctuations in the column oven, such as those caused by the CO\textsubscript{2} cycling. Since temperature variations translate into flow variations, and since the TCD is a flow–sensitive detector, excessive noise resulted.

As noted in Section 4.1.1.4, the maximum column oven temperature that can be employed with the existing column configuration is 250\degree C. Thus, the final column oven temperature was fixed at this value. The analysis was ended after this temperature was reached, as it is unwise to hold the GSQ column at 250\degree C. The temperature programming rate, unlike the initial and final temperatures, was fully optimized. However, as its effect is strongly dependent on the carrier gas flow rates, its value was not set until these rates were well established. In the end, a temperature programming rate of 8\degree C/minute was chosen.

### A.1.2 Carrier Gas Flow Rates

After the temperature variables had been set, optimization of the carrier gas flow rates was conducted. In this study, the main carrier gas flow (Side A) passes through the pyrolysis zone. Thus, it was critical that this flow be maximized so as to achieve adequate quenching of the pyrolysis products. However, if the flow was too high, resolution of the products would have been sacrificed. After a series of runs, the carrier gas flows were set as follows: A (main flow) – 14 mL/min; B (TCD reference flow) – 10 mL/min; Auxiliary (TCD analytical flow) – 10 mL/min. The B and Auxiliary flows were set the same in accordance with TCD operation.
guidelines. No higher than 10 mL/min could pass through the GSQ column without loss of resolution occurring. Fortunately, a higher flow was acceptable for the C\textsubscript{5}+ (FID) analysis.

In order to obtain the flow rates given above, minor changes were made to the Porter carrier gas flow controllers. As the GC was originally designed for packed column usage, the controllers were set to accurately regulate higher helium flow rates than are employed here. As a result, it was deemed necessary to replace the controller cartridges in the B and Auxiliary Porter flow controllers with ones specially designed for capillary column operation. These cartridges provide accurate regulation of helium flows ranging from 0 to 10 mL/min. The A controller cartridge (0–100 mL/min) was not replaced. Incidentally, the controller dial settings were not calibrated to read the actual flow. The actual settings were as follows: A – 159; B – 994; Auxiliary – 872.

A.1.3 Valve Timing

Once the temperature programming and carrier gas flows had been set, the switching of the Valco valve was optimized. The timing was set so that only hydrogen through n–butane passed through to the GSQ column. External relay 3 was programmed to automatically switch the valve at 1.60 minutes. At the end of the run, the valve was automatically switched to the off position in preparation for the next run.
A.1.4 Detectors

The thermal conductivity detector (TCD) is a far less sensitive detector in comparison to the flame ionization detector (FID). Thus, particular attention must be paid to setting its operating parameters. In the current study, the detector was set at the most sensitive range (0.05 mV full-scale); the filament current was subsequently optimized to 177 mA. This corresponded to TCD oven and filament temperatures of 270 and 310°C, respectively. A higher current could have been employed, by setting a larger difference between the TCD oven and TCD filament temperatures. However, a high noise level would have resulted and the filament life would have been drastically reduced.

The flame ionization detector sensitivity is largely a function of the air, hydrogen and make–up helium flows, as well as the detector range setting. Well known recommended values are: air — 300 mL/min; hydrogen — 25 mL/min; and make–up + carrier helium = 30 mL/min. Thus, the make–up flow was set to approximately 16 mL/min. The FID range was varied in accordance with the sample size. When calibrations were conducted, a relatively large sample (0.05 µl) was injected. The most sensitive range that could be employed without voltage over–range was $10^{-10}$ amp/mV. However, for the pyrolysis runs, a range of $10^{-11}$ amp/mV was required just to detect the products, with the exception of the n–hexadecane reactant peak. This peak caused voltage over–ranging at $10^{-11}$ amp/mV. Thus, the analysis was conducted so that the range shifted from $10^{-11}$ to $10^{-10}$ amp/mV just for elution of this one large peak.

In addition to the above FID parameters, the ionization oven temperature
must be set. As a general rule, it should be 50°C hotter than the boiling point of the least volatile major component to ensure that no condensation occurs. In this case, that component was n-hexadecane, which boils at 287°C. Thus, the ionization oven was set to 350°C, to be on the safe side.

A.1.5 Septa

In the current study, the proper choice of the injection port septa is of utmost importance. With most septa on the market, significant bleed (decomposition of the septa material at high injection temperatures) is common. At high sensitivity operation, these contaminants can be of considerable magnitude. This is clearly unacceptable in the current study. Thus, several types of septa were tested until a low bleed type was found. The Pierce Ultra Sep R septa is stable to at least 300°C; thus, low bleed levels were experienced when an injection port temperature of 325°C was maintained.

A.2 GAS CHROMATOGRAPH CALIBRATION

Before, the calibration procedure is described, some aspects should first be clarified.

A.2.1 Theory

The mass response factor is a number by which the peak area (A) has to be multiplied to obtain a measure of the true weight (wt) of the component. These true weights are then normalized to obtain the weight% distribution. The mass
response factor of component i relative to component ref is defined as follows (A - peak area; wt - sample weight):

\[ RF(i) = \frac{A(\text{ref}) \cdot \text{wt}(i)}{A(i) \cdot \text{wt}(\text{ref})} \]  

(A.1)

The response factor of the reference component is set at unity. As the quantification of all the components depends heavily on the choice of the reference component, it should be a prevalent peak that is very well resolved. In this study, ethylene has been chosen as the reference component for the TCD part of the analysis (C\(_4\)-). n-Hexadecane, on the other hand, has been selected as the reference for the FID (C\(_5\)+) analysis. To obtain an overall product distribution (C\(_4\)- and C\(_5\)+ combined), the TCD areas, relative to ethylene, are converted to an equivalent n-hexadecane area by employing factors which take into account the difference between the TCD and FID sensitivities and the ethylene to n-hexadecane FID response. Thus, one obtains all the product areas expressed equivalent to n-hexadecane. If all these areas are then summed, the total should correspond to the n-hexadecane area that would have been measured, had the n-hexadecane not reacted. If the n-hexadecane area/actual weight ratio is known, it can be applied to translate the total area into, say, micrograms. Thus, providing the factors are all accurate, a material balance can be performed.

A.2.2 Procedure and Results

The calibration runs were conducted using GC conditions as close to those employed for the pyrolysis runs, as possible. All parameters given in Table 4.1 remained the same, with the exception of the FID range, as noted in Section A.1.4. Typically, 10 μl gas and 0.05 μl liquid injections were made. Smaller volumes could
not be employed as no very low volume syringes are available.

Numerous hydrocarbon mixtures, ranging from paraffins and olefins to complex polyaromatics, were employed to calibrate the system. A listing of these mixtures and the accompanying weight distributions can be obtained from the author. Many, such as the gas mixtures, were bought already mixed; the suppliers of these are listed in Table A.3. Others were prepared in–house by mixing pure components together in a sealed vial, starting with the higher boiling components first. A digital balance was employed to accurately weigh each component.

Correlation X (Dierickx et al., 1986) was used to calibrate those components for which no pure samples were available. The mass response factors predicted by the correlation fit in well with those determined experimentally. A listing of the mass response factors determined for all expected pyrolysis products, as well as the TCD to FID and ethylene to n–hexadecane factors are given in Table A.1. The components are listed in the order of elution with the C4– (TCD) group first, followed by the C5+ (FID) fraction. The 'Other' groupings refer to components other than the corresponding 1–olefin. They include olefin isomers, diolefins, cyclic olefins and cyclic diolefins.

A.3 MICRO–REACTOR CONSTRUCTION

The construction of the many micro–reactors needed for the pyrolysis studies is a delicate and very time–consuming operation. Thus, the importance of closely following the procedures outlined below cannot be stressed enough. Unless otherwise noted, forceps must be employed at all stages.
Table A.1: Gas Chromatograph Mass Response Factors

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TCD:</strong></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.7784</td>
</tr>
<tr>
<td>Methane</td>
<td>0.7784</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.0000</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.0385</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.1145</td>
</tr>
<tr>
<td>Propane</td>
<td>1.1624</td>
</tr>
<tr>
<td>1-Butene</td>
<td>1.1915</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>1.1521</td>
</tr>
<tr>
<td>t-2-Butene</td>
<td>1.1248</td>
</tr>
<tr>
<td>c-2-Butene</td>
<td>1.0991</td>
</tr>
<tr>
<td><strong>FID:</strong></td>
<td></td>
</tr>
<tr>
<td>1-Pentene</td>
<td>1.1210</td>
</tr>
<tr>
<td>t-2-Pentene</td>
<td>1.1210</td>
</tr>
<tr>
<td>c-2-Pentene</td>
<td>1.1210</td>
</tr>
<tr>
<td>C5 Other</td>
<td>0.9971</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>1.1035</td>
</tr>
<tr>
<td>C5 Other</td>
<td>0.9951</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.8939</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>1.0566</td>
</tr>
<tr>
<td>C7 Other</td>
<td>0.9937</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.9126</td>
</tr>
<tr>
<td>1-Octene</td>
<td>1.0644</td>
</tr>
<tr>
<td>C8 Other</td>
<td>0.9927</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.9213</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.8639</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>0.8639</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.9309</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.9156</td>
</tr>
<tr>
<td>1-Nonene</td>
<td>1.0523</td>
</tr>
<tr>
<td>C9 Other</td>
<td>0.9919</td>
</tr>
<tr>
<td>n-Propylbenzene</td>
<td>0.9388</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>0.9506</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>0.9442</td>
</tr>
<tr>
<td>1-Decene</td>
<td>1.0257</td>
</tr>
<tr>
<td>C10 Other</td>
<td>0.9912</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>0.9365</td>
</tr>
<tr>
<td>Methylstyrene</td>
<td>0.9125</td>
</tr>
</tbody>
</table>

(continued)
Table A.1 (cont’d): Gas Chromatograph Mass Response Factors

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FID (cont’d):</strong></td>
<td></td>
</tr>
<tr>
<td>Indane</td>
<td>0.9530</td>
</tr>
<tr>
<td>Indene</td>
<td>0.9283</td>
</tr>
<tr>
<td>n—Butylbenzene</td>
<td>0.9577</td>
</tr>
<tr>
<td>t—Decalin</td>
<td>0.9447</td>
</tr>
<tr>
<td>Methylindene</td>
<td>0.9122</td>
</tr>
<tr>
<td>1—Undecene</td>
<td>1.0159</td>
</tr>
<tr>
<td>C\textsubscript{11} Other</td>
<td>0.9907</td>
</tr>
<tr>
<td>Tetralin</td>
<td>0.9406</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.9246</td>
</tr>
<tr>
<td>1—Dodecene</td>
<td>1.0054</td>
</tr>
<tr>
<td>C\textsubscript{12} Other</td>
<td>0.9903</td>
</tr>
<tr>
<td>2—Methylnaphthalene</td>
<td>0.8928</td>
</tr>
<tr>
<td>1—Tridecene</td>
<td>1.0126</td>
</tr>
<tr>
<td>C\textsubscript{13} Other</td>
<td>0.9899</td>
</tr>
<tr>
<td>1—Methylnaphthalene</td>
<td>0.8928</td>
</tr>
<tr>
<td>1—Tetradecene</td>
<td>1.0101</td>
</tr>
<tr>
<td>Dimethylnaphthalene</td>
<td>0.9085</td>
</tr>
<tr>
<td>1—Pentadecene</td>
<td>1.0078</td>
</tr>
<tr>
<td>n—Hexadecane</td>
<td>1.0000</td>
</tr>
<tr>
<td><strong>Other:</strong></td>
<td></td>
</tr>
<tr>
<td>Ethylene (TCD to FID)</td>
<td>0.4859</td>
</tr>
<tr>
<td>Ethylene to n—Hexadecane (FID)</td>
<td>1.1509</td>
</tr>
</tbody>
</table>
I. Ferromagnetic Wire Cleaning

The ferromagnetic wires must be cleaned prior to micro-reactor construction to rid them of processing, finger oils, and any other contaminants. The cleaning procedure (Gutteridge et al., 1984) consistently employed is as follows:

1. Place the ferromagnetic wires in a warm (approximately 60°C) 10% v/v hydrochloric acid solution and let sit for 15 minutes.
2. Remove the wires and immediately rinse them in distilled water followed by acetone.
3. Place the wires in a hot (approximately 150°C) vacuum oven and let sit for approximately two hours.
4. When removed, place the wires in a marked, sealed vial.

II. Electrobalance Calibration and Use

1. Before using the Cahn Model 25 Electrobalance, consult the 'Instruction Manual #5728 for Cahn Series—20 Electrobalances'. Non-magnetic forceps must be employed at all times. As well, when using the balance, ensure that you are seated with your elbow resting on the counter. This is critical as your hand must be very stable when placing items to be weighed on the delicate balance pans.
2. Calibrate with the tare on using the 20 mg scale and response level 0. Calibration weights in the 10 to 20 mg range should be employed. The calibration should be repeated daily. At the 20 mg scale, the accuracy is quoted as ±1 μg with a standard deviation of 3 μg.

III. Ferromagnetic Wire Cutting and Weighing Boat Construction

1. Remove the ferromagnetic wires from their storage tube. Then, using small pliers, cut the 86 mm lengths into 7, 12 mm lengths. Place them in a plastic boat and cover.
2. Prepare a compartmentalized tray for storing the prepared micro-reactors and label it accordingly.

3. Construct rectangular (approximately 8 x 5 x 2 mm) weighing boats using the stiff aluminum foil of Fisherbrand aluminum weighing dishes. As the 20 mg range of the Cahn balance is being employed, ensure that the boats each weigh less than 20 mg. Then soak the boats in acetone for a few minutes to remove any finger oils which may be present. Remove them and let dry on a paper towel.

IV. n-Hexadecane Solution

As n-hexadecane is being dissolved in carbon disulfide, a very dangerous solvent, the solution preparation must be conducted in a fume hood, with the door pulled most of the way down. As well, solvent-resistant gloves must be worn.

1. Prepare a solution of approximately 390 µl of n-hexadecane and 100 ml of carbon disulfide. A 100 ml volumetric flask should be employed. The n-hexadecane should be measured using a Hamilton Model #750N liquid syringe. The solution has been designed so that a 5 µl sample contains approximately 15 µg of n-hexadecane.

2. Agitate the solution by inverting the flask and swirling vigorously.

V. Torch and Vacuum Preparation

A natural gas/oxygen torch is employed to seal the micro-reactors. A hot blue flame should be created. Approximate flame dimensions are: outer flame — 5 cm; inner flame — 1 cm.

The vacuum line should be turned on. Ensure that tubing of diameter small enough to seal around the micro-reactor glass is employed.

VI. Micro-reactor Construction

The following procedure should be followed for the construction of each
micro-reactor. Once again, due to the harmful effects of carbon disulfide, all work must be performed in the fume hood, with the exception of the sealing. As well, gloves must be worn. Finally, as very small weights are being recording on the balance, ensure that no fluff or visible dust is present on the boats or wires.

1. Place the weighing boat on the balance using the non-magnetic forceps, record its weight and then tare.

2. Remove the boat and place a ferromagnetic wire in it. Put the boat back on the balance pan and record the wire weight. Meanwhile, agitate the \( n \)-hexadecane solution.

3. Remove the boat/wire from the balance. Withdraw 5 \( \mu l \) of the solution using a Hamilton Model \#7105 liquid syringe. Immediately replace the stopper on the flask. Grasp the wire at the end with the forceps and deposit the solution along the wire in small drops. Tilt the wire up and down to distribute the solution along the length. Within approximately 10 s, the carbon disulfide should be largely evaporated and the wire can be carefully placed back in the boat. Then place the two on the balance pan. Wait a few minutes to ensure that no further evaporation occurs before recording the coated wire weight.

4. Meanwhile, pre-bend the 0.7 mm ID pyrex capillary at approximately 20 mm from one end using the cool outer flame. This prevents the wire from being sucked up the vacuum line.

5. Remove the boat/wire from the balance and place the wire in the 20 mm straight section of the capillary. Place the boat back on the balance.

6. Seal the end through which the wire was inserted in the hot inner flame. Attach the vacuum line to the other end and evacuate the capillary for approximately 60 s.
7. Grasping just in from the sealed end with magnetic forceps, quickly seal the glass right next to the other end of the wire. The vacuum is still hooked up during this procedure. Place the newly formed micro-reactor in the labelled tray. Note that magnetic forceps are employed as they 'hold' the wire, thus eliminating the possibility of dropping the micro-reactor.

8. Record the boat weight. If it is greater than 1 μg, it is likely that some n-hexadecane may have been transferred to the boat. Regardless, remove the boat from the balance and place it in acetone to remove n-hexadecane residue, if any. Check that the negative weight noted for an empty balance pan corresponds to the initial boat weight. Tare the balance in preparation for construction of the next micro-reactor.

A.4 n–HEXADECANE PYROLYSIS PROCEDURE

The n–hexadecane pyrolyses are conducted using a rigid procedure. At the start of each day, it is presumed that the Fischer pyrolyser and timer are off. The Varian 6000 gas chromatograph (GC) should be on with the following temperatures: injection port: 40°C; column oven: 43°C; ionization oven: 200°C; TCD oven: 150°C; and TCD filament: Off. It is critical that the steps outlined below are carried out in exactly the order given.

I. Septum Replacement and Injection Liner Check

1. The existing Pierce Ultra Sep R high–temperature septum located in the Side A injection port nut is replaced. For proper septum conditioning, this must be performed at an injection port temperature not higher than 40°C. Forceps must be employed to avoid contamination of the septum.
As well, the injection port nut should be only slightly hand-tight; do not use a wrench to tighten.

2. Every few days, the Side A column inlet should be disconnected to clean the injection liner. The liner should be flushed with a strong organic solvent, followed by drying in stream of helium. The liner and column inlet should be reconnected following the directions given in the Megabore Conversion Kit instruction booklet. Do not overtighten; the liner and column are very fragile. Before proceeding further, check that the Side A pressure has returned to its initial value (20 - 21 psig).

II. Fischer Heater and GC Warm-up

1. Turn on the Fischer pyrolyser main unit and ensure that the Reaktor dial is programmed to maximum temperature (311°C). Program the GC temperatures as follows: injection port – 325°C; column oven – 33°C; ionization oven – 350°C; and TCD oven – 270°C.

2. When, the TCD oven temperature has reached 270°C (approximately 30 minutes), turn the FID and TCD detector selectors to A and B, respectively. Then program the filament temperature to 310°C. Within, approximately 30 minutes, the filament current will stabilize to 177 mA. In the meantime, turn on the air, medical air and hydrogen cylinders and program the second stage of the regulators to 60, 50 and 40 psig, respectively. The helium cylinder valve should be open at all times, with an outlet pressure of 80 psig. After a few minutes, ignite the FID (Side A).

III. Blank GC Run

Before pyrolyses can be conducted, a blank GC run (i.e. no pyrolysis chamber nor micro-reactor) must be carried out to allow any contaminants within
the gas chromatograph system (i.e. septum, injection liner, columns) to be eluted. In particular, as a new septum is present and the injection port is maintained at a high temperature, some initial septum bleed is expected.

1. Provided the GC is ready (i.e. all temperatures and the filament current have stabilized), the dual channel method stored on the Varian 401 computer can be readied (analysis mode) such that a data link is created between the computer and the GC.

2. Once the Data System ready lights located on the GC panel are illuminated, the GC can be triggered by the Side B automatic start switch (located atop the injection port nut). This will automatically start the GC as well as the data transfer to the Varian 401 computer, on both channels. Note: the TCD (Side B) signal proceeds through Channel 3, while the FID (Side A) signal passes through Channel 1. Approximately one hour will be required to conduct the run and then return the column temperature to its initial value of 33°C.

IV. Blank Baseline Run — Pyrolysis Chamber in Place

1. When the column temperature has fallen to approximately 40°C, place the Fischer pyrolysis reactor module atop the injection block and tighten the adapter ring. Be sure to use gloves as it is very hot. Then ensure that the four pyrolyser mounting posts are placed around the reactor module. Next turn on the timer; ensure that the safety switch is in the down position or else the hammer may drop when the power is turned on. To be on the safe side, also make sure that the hammer is in the down position; it will not drop that way.

2. At this time, the column switching valve should be switched to the on position. This is accomplished by accessing the Time Relay screen on the
GC panel and keying in Relay 3 ON at time 0.00 minutes. As shortly no carrier gas will flow through the Side A injection port, it is critical that the valve position is on so that the TCD is still supplied carrier gas through the auxiliary helium line.

3. Ensure that the hammer seal nut is hand-tight. It should be tight enough to seal around the hammer but not so tight that it restricts the hammer from falling. To check the hammer drop, pull the hammer to the up position (approximately 4 mm below the support top), release the safety switch and depress the trigger. The hammer should drop to within 2 mm of the bottom of the switch contact. Then pull the hammer back up and turn the safety switch back on (down position).

4. Next attach the empty glass pyrolysis chamber to the tee using nylon ferrules. Use a wrench but do not overtighten. Turn the Carrier Gas Switch on the Fischer control unit to the right; this routes the carrier gas through the pyrolysis chamber instead of the gas chromatograph. Let the carrier gas flow through the pyrolysis chamber for a few minutes, to flush out the air. Then measure the flow passing through the end of the pyrolysis chamber needle using a bubble flowmeter. If the Side A Porter flow controller has been set at 159, the flow measured should correspond to approximately 14 mL/min. If the flow is low, check for leaks around the hammer, pyrolysis chamber seal or even at the pyrolysis chamber glass/needle connection.

5. Mount the pyrolysis chamber atop the mounts which surround the Fischer heater. The pyrolysis chamber needle will pass through the injection port septum and into the Megabore injection liner. Thus, flow will now be passing through the gas chromatograph columns. The Side A pressure
should increase to about 12 psig (valve on). If much higher, then the needle has been plugged by the septum. If the needle is plugging often, then either the needle tip design is incorrect or the injection port septum nut has been overtightened. If the Side A pressure is low, then a leak exists in the pyrolysis chamber system. In either case, remove the pyrolysis chamber from the GC, correct the problem and then start again at Step 4.

6. Using the Time Relay screen on the GC panel, turn the switching valve off at time 0.00 min. Within approximately 10 minutes, the Side A pressure A should increase to 20 psig. At this time, connect the bubble flowmeter to the Side B TCD outlet and measure the flow. It should be between 13 and 14 mL/min.

7. Provided the GC is ready (temperatures correct), go to the Varian 401 computer and method ready (MR) the dual channel method. Channel 3 should be in Blank Baseline (B) mode, as a baseline is to be stored for the TCD scan. This is necessary as the valve switch early in the run causes a major jump and then drop in the baseline; this is best subtracted for the pyrolysis runs. Unfortunately, a non-reproducible, and thus difficult to subtract, flow disturbance has been experienced between approximately 6 and 10 minutes. Next, ensure that the Channel 3 RAW data is stored to disk (upper drive), as it may be required at a later date for pyrolysis chromatogram recalculation. Section 7 of the Channel 3 method is modified to permit this. Note that the disk must be pre-formatted using DI (Disk Initialize). Channel 1 (FID A) should be in the analysis mode (A). Although it is not necessary to save a baseline for the FID, this run does allow contaminants within the pyrolysis chamber system to be eluted
prior to the pyrolysis runs.

8. Ensure that the noise level indicated on the Varian 401 SA (System Activity) screen for Channel 3 is less than 30. If not, then the flow has not yet stabilized due to the valve switch. Therefore, the run must be aborted by SO (System Off) of Channel 3.

9. Provided all is well up to this point, release the safety switch on the timer, then depress the trigger button and immediately depress the GC automatic start switch by the Side B injection port nut to start the run.

10. Once the run has been completed (> 30.12 min), remove the pyrolysis chamber from the GC and quickly quickly turn the Fischer Carrier gas switch to the left (off). Then, turn the timer safety switch on (down position). Remove the pyrolysis chamber and inspect it to ensure there are no cracks in the torr—seal due to the heater exposure. Also, check to see if any septum bits are caught in the needle tip. If so, then remove them using gloves, forceps and 32 gauge wire.

V. Pyrolysis Run

An actual pyrolysis run is conducted in much the same manner as the Blank Baseline run described above. The steps below correspond to those given for the Blank Baseline run.

1. This step can be skipped as the heater and mounting posts need not be removed between runs.

2. Perform the procedure given above.

3. The hammer seal nut need only be tightened if an air peak was noted on the previous TCD chromatograph; it would appear at approximately 2.2 minutes. Otherwise, just pull up the hammer.

4. The micro—reactor is first placed in the bottom of the pyrolysis chamber.
Then the pyrolysis chamber is attached to the tee and the rest of the procedure given above is followed.

5. Perform the procedure given above. If many pyrolysis runs have been conducted, an additional reason for low pressure may be that the injection port septum is no longer sealing around the needle. If this is the case, the injection port temperature must be programmed down to 40°C, the filament current turned off, the septum replaced, the filament current turned back on and, finally, the injection port temperature programmed back to 325°C. Once the temperature and current have stabilized, proceed to Stage III.

6. Perform the procedure given above.

7. The procedure given above is followed with a few modifications. Both Channels 3 (TCD B) and 1 (FID A) should be in the analysis (A) mode. As well, RAW data should be stored to disk for both channels (upper drive — Channel 3; lower drive — Channel 1) so that the pyrolysis chromatograms can be recalculated at a later date, if necessary. Section 7 of both of the single channel methods must be modified to permit this.

8. Perform the procedure given above.

9. The procedure given above is to be followed. As well, check that the Side A pressure does not drop to 0 psig after the GC has been started. If it does, this indicates that the pyrolysis chamber has been broken. Immediately turn the TCD filament off, using the Flow/Temp screen, as air will be flowing towards it. Then turn the Fischer carrier gas switch to the left (off). Remove all parts of the broken pyrolysis chamber so that the injection port septum will reseal and the GC will pressure up. Once the Side A pressure has reached approximately 10 psig, program the TCD
filament back to 310°C. Wait until the current has restabilized to 177 mA before beginning again at Step 2. Breakage of the pyrolysis chamber usually occurs due to one of two reasons. The micro-reactor wire may have been forced into the pyrolysis chamber wall by the dropping hammer, thus causing a hole. This can be minimized by filing down the bottom 2 mm of the hammer, so as to achieve a taper. Else, the wire has been forced down into the bottom of the pyrolysis chamber thus weakening and breaking the pyrolysis chamber glass-needle connection. In either case, the pyrolysis chamber is rendered unusable.

10. Follow the procedure given above. Also check the broken micro-reactor to determine if it was sufficiently 'opened' by the hammer to permit easy escape of the products. Normally if at least the top half of the glass (approximately 6 mm) is absent, that is it has been crushed and fallen off, and bottom has been broken open, the micro-reactor has been adequately broken. Otherwise, the products will have remained within the micro-reactor too long and secondary reactions are likely to have occurred. Also visually expect the broken glass and wire to determine if any coke has been deposited. A microscope will be helpful in this regard. Discard the wire and broken glass at this time.

VI. Fischer and GC Shut-down

At the end of the day, a shut-down procedure must be followed.

1. Turn off the Fischer main unit and the timer. For the latter make sure that the safety switch is in the down position. Remove the heater from atop the injection port nut, using gloves.

2. Turn off the filament current (Temp/Flow screen). Then switch off the TCD and FID selectors.
3. Program the temperatures down to those noted before the Stage I procedure. Ensure that the Relay 3 is off at time 0.00; thus, the valve will be in the off position.

4. Turn off the medical air, air and hydrogen main valves. As well, back off the pressure on the second stage and close the line valves for each of these cylinders. Especially for the hydrogen, it is undesirable to have the gas flow running while unattended for long periods of time. Leave the helium cylinder valves untouched; helium must be flowing at all times. The GC columns must not be exposed to air, if it can be helped.

5. Save the Varian 401 methods (dual and two single methods) to disk, as a power failure may occur and clear the computer RAM. Leave the computer on, but turn off the screen.

A.5 MATERIALS AND CHEMICALS

Within this section, the suppliers of the various materials and chemicals employed in this study will be presented in tabular form (Tables A.2 and A.3). In particular, the part numbers and the chemical specifications will be given.
Table A.2: Materials

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<th>Part #</th>
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<td>(Brockville, Ontario)</td>
<td>DB–1 30m x 0.53mm (1.5 μm)</td>
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<td></td>
<td>GSQ 30m x 0.53mm</td>
<td>C20235</td>
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<td>DB–1 15m x 0.53 mm (1.5 μm)</td>
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<td></td>
<td>DB–1 30m x 0.53 mm (5.0 μm)</td>
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<td>Megabore fittings &amp; ferrules:</td>
<td>Kit E conversion kits (2)</td>
<td>C20240</td>
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<td>1/4&quot; detector fitting</td>
<td>C20244</td>
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<td>1/4&quot; direct injection liner</td>
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<td>1/16&quot; fused silica adapters</td>
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<td>1/16&quot; Counter—bored nuts</td>
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<td>1/16&quot; Polyimide ferrules</td>
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<td>Liners for 1/16&quot; FSR (4)</td>
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<td>1 μl liquid (#7001RN)</td>
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<td>25 μl gas (#1702N)</td>
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<td>Houde Glass (Newark, NJ)</td>
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<td>pyrex capillaries</td>
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<td>Alumel</td>
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<td>Omegalaq temperature indicating liquids</td>
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Table A.3: Chemicals

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<td>Fisher Scientific</td>
<td>n—Hexadecane — Certified grade</td>
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<td></td>
<td>ACS grade</td>
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<td>Acetone — Certified ACS</td>
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<td>Matheson Gas</td>
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<td>(Edmonton, AB)</td>
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<td><strong>Calibration Standards:</strong></td>
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<td>Mandel Scientific</td>
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<td>Gas oil RFC Mixture</td>
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APPENDIX B
EXPERIMENTAL DATA

In this appendix, the n-hexadecane pyrolysis data obtained from the micro-reaction system experiments, under conditions of 576 to 842°C and 100 to 3200 ms, are presented. Although, only seventeen runs are presented, many more were actually performed. Some were replicates of the data already given; others were discarded due to experimental problems, such as improper micro-reactor glass fracture, excessive FID contamination, etc. All in all, approximately sixty n-hexadecane pyrolysis runs were actually conducted.

As noted in Tables B.1, B.2, B.3 and B.4, the actual reaction time, n-hexadecane conversion, weight, pressures and, in particular, the product distribution, are tabulated for each run. The pyrolysis time corresponds to that value which was read off the timer control unit display. The n-hexadecane weight is that which was determined through chromatography, as the Cahn electrobalance weights were highly erroneous. As outlined in Section 2.5.2, pyrolysis is not an equimolar reaction; hence additional moles are formed as the reaction proceeds. As the volume of the reactor is fixed, a pressure increase was noted.

The material balance is actually a hydrogen to carbon molar ratio comparison between the n-hexadecane feed (H/C=2.125) and the pyrolysis products. If the hydrogen to carbon ratio of the products was less than that of n-hexadecane, a material balance of less than 100% resulted. Conversely, if higher ratios occurred, the material balance exceeded 100%. The deviations from perfect
material balance closure are due to slight inaccuracies in the gas chromatography analysis. The $C_4$—content, in particular, is suspected to be slightly imprecise due to the problems encountered with the thermal conductivity detector, as outlined in Section 5.3.1.

The product distribution data has been tabulated in the order that the components eluted from the gas chromatography system. Due to the fact that non—polar separating phases were employed, the most volatile components eluted first with the high—boiling $n$—hexadecane eluting last. All the components listed are self—explanatory, with the exception of the $C_x$ Other fractions (where $x = 5$ to 13). These groupings include compounds other than the 1—olefin ($1—C_xH_{2x}$), such as olefin isomers, diolefins, cyclic olefins and cyclic diolefins.
Table B.1: n-Hexadecane Pyrolysis Data — 576°C

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<th>Reaction time (ms):</th>
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<td>n-Hexadecane Conversion (%)</td>
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Table B.2: n-Hexadecane Pyrolysis Data — 750°C

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<td>45.46</td>
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Table B.3: n-Hexadecane Pyrolysis Data — 750°C Gold-plated

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</tr>
<tr>
<td>1,3-Butadiene</td>
<td>—</td>
<td>0.669</td>
<td>2.070</td>
</tr>
<tr>
<td>t-2-Butene</td>
<td>—</td>
<td>—</td>
<td>0.091</td>
</tr>
<tr>
<td>c-2-Butene</td>
<td>—</td>
<td>—</td>
<td>0.171</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>0.230</td>
<td>3.303</td>
<td>3.891</td>
</tr>
<tr>
<td>t-2-Pentene</td>
<td>—</td>
<td>0.190</td>
<td>0.521</td>
</tr>
<tr>
<td>c-2-Pentene</td>
<td>0.015</td>
<td>0.199</td>
<td>0.742</td>
</tr>
<tr>
<td>C5 Other</td>
<td>0.049</td>
<td>0.639</td>
<td>1.543</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>0.329</td>
<td>4.318</td>
<td>3.724</td>
</tr>
<tr>
<td>C6 Other</td>
<td>—</td>
<td>0.729</td>
<td>1.902</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.027</td>
<td>0.205</td>
<td>0.610</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>0.201</td>
<td>2.284</td>
<td>3.181</td>
</tr>
<tr>
<td>C7 Other</td>
<td>0.014</td>
<td>0.302</td>
<td>0.783</td>
</tr>
<tr>
<td>Toluene</td>
<td>trace</td>
<td>0.060</td>
<td>0.259</td>
</tr>
<tr>
<td>1-Octene</td>
<td>0.168</td>
<td>1.888</td>
<td>2.763</td>
</tr>
<tr>
<td>C8 Other</td>
<td>0.014</td>
<td>0.126</td>
<td>0.320</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>—</td>
<td>0.014</td>
<td>0.046</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>—</td>
<td>—</td>
<td>0.031</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>—</td>
<td>—</td>
<td>0.010</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.013</td>
<td>0.028</td>
<td>0.154</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>—</td>
<td>0.055</td>
<td>—</td>
</tr>
<tr>
<td>1-Nonene</td>
<td>0.165</td>
<td>1.791</td>
<td>2.940</td>
</tr>
<tr>
<td>C9 Other</td>
<td>—</td>
<td>0.069</td>
<td>0.144</td>
</tr>
<tr>
<td>n-Propylbenzene</td>
<td>—</td>
<td>—</td>
<td>0.036</td>
</tr>
<tr>
<td>1-Decene</td>
<td>0.180</td>
<td>1.826</td>
<td>2.905</td>
</tr>
<tr>
<td>C10 Other</td>
<td>—</td>
<td>0.073</td>
<td>0.094</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>—</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>0.020</td>
<td>0.020</td>
<td>0.016</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>—</td>
<td>—</td>
<td>0.015</td>
</tr>
<tr>
<td>Indene</td>
<td>—</td>
<td>—</td>
<td>0.018</td>
</tr>
<tr>
<td>n-Butylbenzene</td>
<td>—</td>
<td>—</td>
<td>0.019</td>
</tr>
</tbody>
</table>

(continued)
Table B.3 (cont’d): n-Hexadecane Pyrolysis Data – 750°C Gold-plated

<table>
<thead>
<tr>
<th>Reaction time (ms):</th>
<th>99</th>
<th>498</th>
<th>1097</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexadecane Conversion (%):</td>
<td>5.68</td>
<td>44.66</td>
<td>68.04</td>
</tr>
<tr>
<td>Product Distribution (wt%):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-Decalin</td>
<td>—</td>
<td>—</td>
<td>0.015</td>
</tr>
<tr>
<td>Methylindene</td>
<td>0.033</td>
<td>0.026</td>
<td>—</td>
</tr>
<tr>
<td>1—Undecene</td>
<td>0.165</td>
<td>1.622</td>
<td>2.795</td>
</tr>
<tr>
<td>C₁₁ Other</td>
<td>—</td>
<td>0.046</td>
<td>0.092</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>—</td>
<td>0.018</td>
<td>0.039</td>
</tr>
<tr>
<td>1—Dodecene</td>
<td>0.204</td>
<td>1.586</td>
<td>2.211</td>
</tr>
<tr>
<td>C₁₂ Other</td>
<td>—</td>
<td>0.034</td>
<td>0.020</td>
</tr>
<tr>
<td>2—Methylnaphthalene</td>
<td>—</td>
<td>0.016</td>
<td>—</td>
</tr>
<tr>
<td>1—Tridecene</td>
<td>0.210</td>
<td>1.488</td>
<td>1.668</td>
</tr>
<tr>
<td>C₁₃ Other</td>
<td>—</td>
<td>0.019</td>
<td>0.013</td>
</tr>
<tr>
<td>Dimethylnaphthalene</td>
<td>—</td>
<td>0.024</td>
<td>—</td>
</tr>
<tr>
<td>1—Tetradecene</td>
<td>0.182</td>
<td>1.323</td>
<td>1.140</td>
</tr>
<tr>
<td>1—Pentadecene</td>
<td>0.088</td>
<td>0.606</td>
<td>0.767</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>94.323</td>
<td>55.336</td>
<td>31.959</td>
</tr>
<tr>
<td></td>
<td>100.000</td>
<td>100.000</td>
<td>99.999</td>
</tr>
</tbody>
</table>
Table B.4: n-Hexadecane Pyrolysis Data — 842°C

<table>
<thead>
<tr>
<th>Reaction time (ms):</th>
<th>97</th>
<th>243</th>
<th>500</th>
<th>795</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexadecane Conversion (%):</td>
<td>10.65</td>
<td>46.97</td>
<td>86.62</td>
<td>91.78</td>
</tr>
<tr>
<td>n-Hexadecane Weight (µg):</td>
<td>7.8</td>
<td>12.1</td>
<td>7.7</td>
<td>10.2</td>
</tr>
<tr>
<td>Material Balance (%):</td>
<td>95.7</td>
<td>111.7</td>
<td>101.8</td>
<td>104.4</td>
</tr>
<tr>
<td>Pressures (atm): Initial</td>
<td>1.01</td>
<td>1.57</td>
<td>1.00</td>
<td>1.33</td>
</tr>
<tr>
<td>Final</td>
<td>1.35</td>
<td>5.49</td>
<td>5.88</td>
<td>8.40</td>
</tr>
</tbody>
</table>

Product Distribution (wt%):

| Hydrogen | 0.022 | 0.215 | 0.308 | 0.420 |
| Methane  | 0.525 | 5.083 | 7.268 | 9.903 |
| Ethylene | 1.580 | 11.544 | 27.647 | 27.725 |
| Acetylene | — | — | trace | trace |
| Ethane   | 0.385 | 1.947 | 5.037 | 6.966 |
| Propylene | 0.632 | 5.670 | 13.579 | 11.530 |
| Propane  | 0.026 | 0.237 | 0.566 | 0.481 |
| 1-Butene | 0.255 | 2.706 | 3.915 | 2.730 |
| 1,3-Butadiene | — | 1.763 | 4.422 | 3.780 |
| t-2-Butene | — | 0.147 | 0.536 | 0.673 |
| c-2-Butene | — | 0.044 | 0.510 | 0.341 |
| 1-Pentene | 0.526 | 2.911 | 2.605 | 1.515 |
| t-2-Pentene | — | 0.288 | 0.808 | 0.823 |
| C5 Other | 0.031 | 0.454 | 2.064 | 2.478 |
| 1-Hexene  | 0.220 | 1.109 | 2.316 | 1.956 |
| C6 Other  | 0.720 | 2.563 | 1.637 | 0.768 |
| Benzene   | 0.044 | 0.956 | 2.683 | 1.965 |
| 1-Heptene | 0.165 | 0.226 | 2.110 | 4.351 |
| C7 Other  | 0.436 | 1.329 | 0.754 | 0.361 |
| Toluene   | 0.083 | 0.256 | 0.622 | 0.397 |
| 1-Octene  | 0.045 | 0.082 | 0.724 | 1.803 |
| C8 Other  | 0.402 | 1.029 | 0.550 | 0.408 |
| Ethylbenzene | 0.224 | 0.132 | 0.089 | 0.311 |
| p-Xylene  | 0.111 | 0.023 | 0.091 | 0.303 |
| m-Xylene  | 0.055 | 0.013 | 0.062 | 0.199 |
| Styrene   | 0.059 | — | — | 0.035 |
| o-Xylene  | 0.141 | 0.019 | 0.262 | 0.719 |
| 1-Nonene  | 0.062 | 0.049 | 0.047 | 0.169 |
| C9 Other  | 0.453 | 0.924 | 0.521 | 0.613 |
| n-Propylbenzene | — | — | 0.028 | 0.138 |
| 1-Decene  | 0.583 | 0.924 | 0.492 | 0.422 |
| C10 Other | — | 0.132 | 0.090 | 0.456 |
| 1,2,3-Trimethylbenzene | — | — | 0.033 | 0.292 |
| Indane    | — | — | — | 0.134 |
| Indene    | — | — | 1.105 | 0.440 |
| n-Butylbenzene | — | — | — | 0.149 |
| t-Decalin | — | 0.023 | — | — |

(continued)
Table B.4 (cont’d): n–Hexadecane Pyrolysis Data — 842°C

<table>
<thead>
<tr>
<th>Reaction time (ms):</th>
<th>97</th>
<th>243</th>
<th>500</th>
<th>795</th>
</tr>
</thead>
<tbody>
<tr>
<td>n–Hexadecane Conversion (%):</td>
<td>10.65</td>
<td>46.97</td>
<td>86.62</td>
<td>91.78</td>
</tr>
<tr>
<td>Product Distribution (wt%):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylindene</td>
<td>—</td>
<td>0.019</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1–Undecene</td>
<td>0.594</td>
<td>0.777</td>
<td>0.428</td>
<td>0.489</td>
</tr>
<tr>
<td>C11 Other</td>
<td>—</td>
<td>0.061</td>
<td>0.157</td>
<td>0.886</td>
</tr>
<tr>
<td>Tetralin</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.218</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>—</td>
<td>0.159</td>
<td>0.119</td>
<td>0.530</td>
</tr>
<tr>
<td>1–Dodecene</td>
<td>0.837</td>
<td>0.753</td>
<td>0.415</td>
<td>0.414</td>
</tr>
<tr>
<td>C12 Other</td>
<td>—</td>
<td>0.284</td>
<td>0.134</td>
<td>1.163</td>
</tr>
<tr>
<td>2–Methylnaphthalene</td>
<td>—</td>
<td>0.113</td>
<td>0.115</td>
<td>0.270</td>
</tr>
<tr>
<td>1–Tridecene</td>
<td>0.783</td>
<td>0.735</td>
<td>0.491</td>
<td>0.432</td>
</tr>
<tr>
<td>C13 Other</td>
<td>—</td>
<td>0.037</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1–Methylnaphthalene</td>
<td>—</td>
<td>—</td>
<td>0.128</td>
<td>0.296</td>
</tr>
<tr>
<td>1–Tetradecene</td>
<td>0.075</td>
<td>0.729</td>
<td>0.600</td>
<td>0.436</td>
</tr>
<tr>
<td>1–Pentadecene</td>
<td>0.579</td>
<td>0.507</td>
<td>0.550</td>
<td>0.259</td>
</tr>
<tr>
<td>n–Hexadecane</td>
<td>99.998</td>
<td>100.002</td>
<td>99.999</td>
<td>99.998</td>
</tr>
</tbody>
</table>
In this appendix, the Advanced Continuous Simulation Language (ACSL) fortran code, which was employed to simulate the dynamic thermal behaviour of the micro-reactor, is given. The equations pertaining to the simulation have been presented in Section 5.1.2. As the program has been fairly well-documented, there is no need to elaborate any further.
Program Unsteady

"This ACSL program simulates the dynamic thermal response of the n—hexadecane pyrolysis micro—reactor."

Written by: Judy A. Fairburn

Last Modified: March 17, 1988

"Define constants:"
constant r1 = 0.20e−3 $wire radius (m)$
constant r2 = 0.35e−3 $capillary inside radius (m)$
constant t0 = 543.15 $initial/ambient temperature (K)$
constant tf = 1115.15 $final temperature (K)$
constant tmf = 2.0 $simulation end time (s)$
constant m1 = 10 $number of grid points$
constant mw = 226.448 $n—C16 molecular weight$
constant tc = 717.0 $n—C16 critical temperature (K)$
constant pc = 14.0 $n—C16 critical pressure (atm)$
constant rho1 = 4.823 $n—C16 density — 15μg (kg/m3)$
constant u2 = 54.1 $overall h.t. coeff. (W/m2 K)$

"Define independent variable, variable types and array dimension:"
variable tm = 0.0
integer i, m1, n1
array t1(11), ti(11), dt1dtm(11), k1(11), cp1(11), al1(11),...
    rrl(11), dk1dt(11)
array ft1(10), ft1(10), fdl1dt(10)
n1 = m1 + 1

"Set initial conditions:"
do 5 i=2,n1
    ti(i) = t0
    ft(i−1) = ti(i)
5..continue

"Computed constants:"
k1con = tc**(1./6.) * mw**(1./2.) / pc**(2./3.)
dr1 = (r2 − r1) / m1

"Compute radii vectors:"
do 15 i=1,n1
    rrl(i) = (i−1) * dr1 + r1
15..continue

***************
End "$\text{initial}"
***************

************
Dynamic
************

"Compute wire surface temperature (K) -- b.c. at r1:"
  if (tm \leq 0.0) t1(1) = t0
  t1(1) = tf

"Compute temperature dependent properties in region:"
do 25 i=2,n1
  cp1(i) = 4186.8/mw * (-3.109 + 0.3652*t1(i)...
                - 2.039e-4*t1(i)**2.0 + 4.418e-8*t1(i)**3.0)
  tr = t1(i) / tc
  kla = (-0.152*tr + 1.191*tr**2.0 - 0.039*tr**3.0) * 73.12e-5
  k1b = 99.6e-6 * (exp(0.0464*tr) - exp(-0.2412*tr))
  k1(i) = (k1a + k1b) * 418.68 / k1con
  all(i) = k1(i) / (rho1 * cp1(i))
  dtrdt = 1.0 / tc
  dk1a = 99.6e-6 * (0.0464*exp(0.0464*tr) + 0.2412*exp(-0.2412*tr))
  dk1b = 73.12e-5 * (-0.152 + 2.382*tr - 0.117*tr**2.0)
  dk1dt(i) = dtrdt * (dk1a + dk1b) * 418.68 / k1con
25..continue

"Compute thermal gradients inside region:"
do 30 i=2,m1
  dt1a = k1(i) / dr1**2.0 * (t1(i+1) - 2.0*t1(i) + t1(i-1))
  dt1b = dk1dt(i) * ((t1(i+1) - t1(i-1)) / (2.0 * dr1))**2.0
  dt1c = k1(i) / (2.0 * rr1(i)*dr1) * (t1(i+1) - t1(i-1))
  dt1dtm(i) = (dt1a + dt1b + dt1c) / (rho1 * cp1(i))
  dtd1dt(i-1) = dt1dtm(i)
30..continue

"Compute thermal gradient at radius r2 -- convective b.c.:
  dtd1dtm(n1) = 2.0*all(n1)*((t1(m1)-t1(n1))/dr1**2.0-u2/(dr1*k1(n1))...
                          *(t1(n1)-t0) + (t1(n1)-t1(m1))/(2.0*r2*dr1))
  fdt1dt(m1) = dtd1dtm(n1)

***************
Derivative
***************

"Define integration parameters:"
cinterval cint = 0.000001
algorithm ialg = 2
nsteps nstp = 1
merror merr = 0.01
xerror \quad xerr = 0.01

"Integrate temperature vector:"
procedural (t1 = i, n1, fd1dt, fti1)
\quad ft1 = intvc (fdt1dt, fti1)
\quad do 40 i=2,n1
\quad \quad ti(i) = ft1(i-1)
40..continue
end

!!!
End "$derivative"
!!!

"Termination condition:"
\quad termt (tm .ge. tmf)

!!!
End "$dynamic"
!!!

!!!
Terminal
End "$terminal"
!!!

End "$program"