### UNIVERSITY OF CALGARY

Thermal Cracking of Gas Oil in a Helical Coil Reactor

by

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A THESIS

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#### Abstract

Hydrotreated light gas oil derived from Athabasca bitumen has several properties, which make it a less desirable transportation fuel. Its boiling point is in the range of diesel, which is too high to be used as gasoline. However, the gas oil also has a significant amount of fused ring compounds, which makes its cetane number too low for diesel specifications. Thermal cracking (pyrolysis) is one of the simplest and economically the most important upgrading reactions in industrial application. It was expected that the thermal cracking method could significantly upgrade the gas oil to naphtha.

A previously designed helical coil reaction system was modified and employed to thermally crack light gas oil to produce naphtha. Thermal cracking of hydrotreated light gas oil was studied at three different temperature levels, 500°C, 530°C and 550°C. Extents of cracking or conversions of LGO for experiments were in the range of 15% to 46%.

For the purposes of comparing current results to the literature, a kinetic analysis assuming a first order overall decomposition model for the light gas oil thermal cracking reaction was examined. The activation energy of this overall reaction was evaluated at 153 kJ/mol. The light gas oil feed used in this study has an estimated average molecular weight of 212. The activation energy found in this study was very close to that of n-

hexadecane (molecular weight of 226) determined by previous researchers (Fairburn et al., 1990, activation energy of 164 kJ/mol).

A more detailed reaction network involving a four-lump kinetic model was proposed. Lumps were chosen in order to give a better understanding of the product distribution. According to the experimental data, the activation energy for the reaction of gas oil to naphtha was 173 kJ/mol, for the reaction of gas oil to gas was 83 kJ/mol, for the reaction of naphtha to gas was 215 kJ/mol and for the reaction of gas oil to coke was 262 kJ/mol. The activation energy for the reaction of naphtha to gas is close to 220.8 kJ/mol obtained by Kumar and Kunzru (1985) and within the range of 212 to 228 kJ/mol found by van Damme and Froment (1981). From the proposed model, a set of optimal reaction times at different temperatures is predicted.

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## Nomenclature

A	cross-section area of the reactor tube, m <sup>2</sup>
Aj	frequency factor for reaction j, s <sup>-1</sup>
C <sub>p</sub>	heat capacity of reaction fluid, J/kgK
d	reactor tube ID, m
Ej	activation energy for reaction j, J/mol
f	friction factor
G	fluid mass flux, kg/m <sup>2</sup> ·s
h	heat transfer coefficient, W/m <sup>2</sup> K
k	thermal conductivity, W/mK
k1, k2, k3, k4	first order rate constants for reactions 1, 2, 3, 4, $s^{-1}$
kj	first order rate constant for reaction j (j=1, 2, 3, 4), $s^{-1}$
ko	first order rate constant for the overall reaction, s <sup>-1</sup>
<b>k</b> (T)	reaction constant in Equation (2.1)
<i>m</i>	feed mass flow rate, g/s
m <sub>C5+</sub>	mass of pentene and heavier hydrocarbons, g
m <sub>coke</sub>	mass of coke pseudo-component, g
Mdemister	demister weight increase after experiment, which is included in
	the mass of naphtha pseudo-component, g
m <sub>gas</sub>	mass of gas pseudo-component, g
m <sub>gasoil</sub>	mass of gas oil pseudo-component, g

mliquid	mass of liquid product, g
m <sub>парhtha</sub>	mass of naphtha pseudo-component, g
$\overline{M}$	average molecular weight of inlet feed and outlet product, g/mol
Mi	molecular weight of component i in the gas bag, g/mol
n	order of the reaction in Equation (2.1)
Nu	Nusselt number
P	reaction pressure, Pa
Pr	Prandtl number
R	gas constant, J/mol K
Re	Reynolds number, dup/µ
t	residence time, s
t <sub>1/2</sub>	reaction half-life, s
Т	reaction temperature, K
To	room temperature, K
u	fluid velocity, m/s
ν	volumetric flow rate at reactor conditions, m <sup>3</sup> /s
v <sub>N2</sub>	nitrogen volumetric flow rate at room temperature, m <sup>3</sup> /s
v	reactor volume, m <sup>3</sup>
$V_{gasbag}$	volume of gas bag, recorded by wet test meter, m <sup>3</sup>
x <sub>10</sub> , x <sub>20</sub>	initial (feed) weight percent of pseudo components 1 (naphtha)
	and 2 (LGO)

x <sub>1</sub> , x <sub>2</sub> , x <sub>3</sub> , x <sub>4</sub> weight percent of pseudo-component 1 (naphtha), 2	
	3 (gas), 4 (coke)
Х	a property of the feed in Equation (2.1)
Ynaphtha	naphtha pseudo-component mass fraction from SimDist
Ygasoil	gas oil pseudo-component mass fraction from SimDist
Y <sub>CO2</sub>	CO <sub>2</sub> volume percent in the gas bag
Y <sub>i</sub>	volume percent of component i in the gas bag

## Greek

μ	fluid viscosity, Pa·s
ρ	fluid density, kg/m <sup>3</sup>

### Abbreviations

ASTM	American Society for Testing and Materials
С	Coke
G	Gas
GC	Gas Chromatograph
НО	Hydraulic Oil
HP	Hewlett-Packard
ICFB	Internally Circulating Fluidized Bed

ID	Inside Diameter	
L	Liquid	
LGO	Light Gas Oil	
LHSV	Liquid Hourly Space Velocity	
MS	Mass Spectrophometer	
MW	Molecular Weight	
PFR	Plug Flow Reactor	
SimDist	Simulated Distillation	
TCD	Thermal Conductivity Detector	
WTM	Wet Test Meter	

### CHAPTER 1

#### **Introduction and Objectives**

### 1.1 Introduction

Oil sand is composed of sand, bitumen, mineral rich clays and water. In its raw state, bitumen is a black, asphalt-like oil. It requires upgrading to make it transportable by pipeline and usable by conventional refineries. The upgraded bitumen product consists of naphtha, light and heavy gas oils that are combined to produce a light, sweet crude oil.

The oil sands deposits in Alberta are estimated to contain over 1.7 trillion barrels - more than five times larger than Saudi Arabia's hydrocarbon reserves. As Canada's conventional reserves of light and medium oil continue to diminish while consumption rises, the need for such an alternative oil source is apparent. (Syncrude Canada Ltd., 2000b)

In the Syncrude Canada oil sand plant at Fort McMurray, bitumen is fed into either one of two cokers or a hydroprocessing unit. It is thermally cracked into hydrocarbon gases, naphtha and gas oil. While the hydrocarbon gases are treated for use as refinery fuel, the naphtha and gas oils are treated and blended into sweet blend crude oil. The oil is then transported via pipeline to refineries in Edmonton, eastern Canada and the mid-western United States.

Coking processes have been selected by many refiners as their preferred choice for bottom of the barrel upgrading, because the process has the inherent flexibility to handle even the heaviest of residues. The process provides essentially complete rejection of metals while providing partial conversion to naphtha and diesel cuts.

The valuable products of the coker are naphtha and gas oil; the by-products are fuel gases and coke. The coker naphtha and gas oil are unstable because they contain relatively high quantities of sulfur, nitrogen and unsaturates. Naphtha and gas oil streams are sent to catalytic hydrotreating units to turn nitrogen into ammonia and sulfur to hydrogen sulfide and to stabilize or saturate the unsaturates.

However, to utilize the hydrotreated gas oil derived from Athabasca bitumen is difficult. Its boiling point is in the range of diesel, however, the synthetic crude diesel fraction has a cetane number of 34 (Yui, 1999), which is too low for diesel specifications. The minimum cetane number required for a general purpose, middle distillate fuel for automotive diesel engines is 40 (ASTM D975, 1998). The low cetane number of the bitumen derived gas oil fraction is caused by a significant amount of fused ring compounds. Table 1.1 shows properties of the light gas oil fraction of Syncrude Sweet Blend (Yui, 1999).

# Table 1.1 Typical Properties of the Light Gas Oil Fraction

# of Syncrude Sweet Blend (Yui, 1999)

Property	Light Gas Oil	
Density at 15°C, g/ml	0.878	
Carbon, wt%	87.7	
Hydrogen, wt%	12.1	
Nitrogen, wppm	99	
Sulfur, wt%	0.023	
Aniline Point, °C	47	
Aromatics (Supercritical Fluid	42.2	
Chromatography), wt%		
Cetane Number	34.0	
Kinematic Viscosity at 20°C, cSt	5.3	

Hydrocarbon cracking is the process by which higher molecular weight hydrocarbons are converted to lower molecular weight hydrocarbons through carbon-carbon bond scission. There are three general types of hydrocarbon cracking: thermal cracking, catalytic cracking, and hydrocracking. Each process has its own characteristics concerning reaction conditions and product compositions. Among them, hydrocarbon thermal cracking (pyrolysis) is the simplest and economically the most important industrial reaction. A wide spectrum of feedstock, ranging from ethane to vacuum gas oil, is pyrolyzed to produce olefins vital to the petrochemical industry. Thermal cracking has also been applied to the upgrading of bitumen or heavy oil. At present, a total daily production of about 330,000 barrels of upgraded oil has been achieved at the northern Alberta oil sand plants. It is expected that after on-going expansion projects, a daily production of 830,000 barrels may be reached in 2008 (Syncrude Canada Ltd, 2000a and Suncor Energy Inc., 2000).

### 1.2 Objectives

The objective of this work is to study thermal cracking reactions of hydrotreated light gas oil for production of liquid products over the temperature of 500 tc. 550°C. This temperature range was chosen as it is within the range of reactor temperatures for fluid coking (Kunii and Levenspiel, 1991). The experiments were also designed to obtain measurable quantities of all products. For a range of operating conditions, yield of products, especially naphtha, will be measured. Lumped reaction kinetics will be determined and using the experimentally determined kinetic parameters, the effect of reaction temperature and residence time on the optimal production of naphtha will be investigated.

### CHAPTER 2

#### Literature Review

Thermal cracking reactions of hydrocarbons have been of great interest to chemists even before the petroleum industry began. The industry of producing chemicals from petroleum started when chemists in the 1920's produced alcohols from ethylene and propylene via thermal cracking (Stolfa, 1980). From this point, thermal processes for the production of basic chemical feedstocks: ethene, propylene, butenes, butadiene and aromatics, have been increasingly important. Nowadays a vast industry throughout the world is based on olefins and aromatics produced by thermal reactions of hydrocarbons. The by-products, such as coke and gas, are available as commercial items and all are produced by thermal means. Thermal reactions are still playing an important role in the production of hydrocarbons from shale, oil sands, coal and lignite.

Before a kinetic study of light gas oil (LGO) thermal cracking can be initiated, a good understanding of the industrial and the theoretical aspects of hydrocarbon thermal cracking is essential.

### 2.1 Industrial Applications of Thermal Cracking Reactions

The thermal processing technologies in the petroleum refining industry refers to the upgrading method that utilizes heat to initiate reactions of feedstocks. Thermal cracking is distinct from other processes such as catalytic and solvent processes. Thermal processes have good flexibility for different feeds because the reactions depend only on heat effects without the need for catalyst or solvent. Thermal processes can deal with residues as well as distillate oil, and can treat "cleaner" feed or feed with large amounts of impurities (sulfur, nitrogen, oxygen, heavy metals, asphaltenes, etc.).

One of the purposes of heavy oil thermal processing is to convert the heavy end of the crude, including vacuum distillate and residue, into useable products. For example, to turn high viscosity, high pour point vacuum residue into fuel oil. However, the more important aspect is upgrading, to transform low value heavy oil into valuable light oils.

Although facing competition from other processes, thermal processes remain important. The following processes are used by many refineries (Cheng, 1994):

- low severity visbreaking to produce fuel oil from atmospheric or vacuum residue;
- (2) thermal cracking to produce gasoline, diesel and fuel oil from gas oil;
- (3) coking to produce gasoline, diesel, gas oil and coke from vacuum residue.

Table 2.1 shows some of the thermal operations used in industry (Stolfa, 1980). In contemporary petroleum refining industry, the thermal processes tend to have larger capacity, simpler operation, and lower utility costs. These are the essential points that help the modern thermal processes survive and continue developing.

# Table 2.1 Thermal Processing for the Purpose of Hydrocarbons Upgrading

Operation	Feed	Products
1. Thermal cracking	Gas oil, decant oil,	Gas, gasoline, thermal tar
	furfural extract,	
	coker gas oil,	
	or vacuum gas oil	
	Atmospheric bottoms	Gas, gasoline, middle distillate,
		fuel oil
2. Visbreaking	Atmospheric bottoms	Gas, gasoline, fuel oil
	Atmospheric bottoms	Gas, gasoline, middle distillate,
		fuel oil
	Atmospheric bottoms	Gas, gasoline, middle distillate,
		vacuum gas oil, vacuum bottoms
	Vacuum bottoms	Gas, gasoline, middle distillate,
		fuel oil
3. Visbreaking &	Atmospheric bottoms	Gas, gasoline, middle distillate,
gas oil cracking		vacuum bottoms
4. Coking	Atmospheric bottoms	Gas, gasoline, middle distillate,
(partial recycle)		coke
5. Coking	Atmospheric bottoms	Gas, gasoline, middle distillate,
(low pressure)	or vacuum bottoms	heavy coker gas oil, coke

(adapted from Stolfa, 1980)

### 2.2 Pilot Reactors

Pilot reactors are scale down units of a commercial or potentially commercial process designed to test a particular process. They are designed based on kinetics obtained from laboratory or bench scale reactors similar to those obtained in this study. Two examples of pilot scale thermal cracking reactors are given below.

A fast pyrolysis reactor called the thermovortactor has been developed at the University of Western Ontario for heavy hydrocarbon thermal cracking. Vogiatzis *et al.* (1988) used this reactor to study the pyrolysis of Cold Lake heavy oil. In this reactor, high temperature nitrogen and preheated heavy oil feed are rapidly mixed in a cyclone-like device prior to entering a reaction tube. The pyrolysis products exiting the reaction tube are quenched with liquid nitrogen in a second cyclone-like device called a cryovortactor. The system is capable of achieving temperature in the range of 550-580°C and residence time of 100-500 ms.

Milne *et al.* (1992, 1999) developed an internally circulating fluidized bed (ICFB) reactor. The ICFB is a modification to the gas spouted bed. The main advantage of this design is that the ICFB successfully and simultaneously overcomes gas bypassing and high temperature instability of gas spouted bed. With a pilot scale facility, heavy oil pyrolysis experiments were carried out and it is shown that the ICFB reactor is capable of achieving the high temperature (800°C) and short reaction time (450 ms) required to

minimize coke by-product formation in the thermal conversion of heavy oils to olefins and light liquids (Milne et al., 1994).

With pilot scale results, the next step is a demonstration unit, which is designed to show that a process can operate at near to commercial scale. Kinetics from studies such as this one are useful for reactor modelling at all scales of operation: pilot, demonstration and commercial. However, the laboratory reactors used for kinetic studies do not necessarily resemble the commercial unit and for good reason. Residence time and temperature must be more tightly controlled than is possible with a scale down unit.

### 2.3 Laboratory Reactors for Thermal Cracking Kinetic Studies

Chemical kinetic study is a very important approach to analyze the rates of chemical transformations and predict rates of reactions under new conditions. A proper kinetic model combined with suitable reactor model can predict performance for industrial scale production.

Proper design of the reactor is crucial to a kinetic study. When intrinsic rate equations are not available, experimental data is required. It is preferred to obtain these data from a bench-scale laboratory reactor, rather than from a pilot plant or commercial-scale reactor. The reason for this is with a laboratory reactor, the design as well as operating conditions can be chosen to reduce or eliminate the effects of mass and heat transfer. It

should also be noted that these bench scale reactors suitable for kinetic studies are not scale-down versions of units in commercial operation but often designed especially to obtain kinetic data.

The following are different types of reactors that have been used to study kinetics of hydrocarbon thermal cracking. The advantages and restrictions of each type of reactor are reviewed.

### 2.3.1 Batch Reactors

Before 1970's, most laboratory gas-phase pyrolyses of hydrocarbons were carried out in batch reactors. However, they are seldom employed on a commercial scale as productivities are low.

### **2.3.1.1 Conventional Batch Reactors**

In a conventional batch reactor, the reactant is placed in a closed vessel and pyrolyzed under constant volume conditions. The reactor is usually made of high temperature glasses such as quartz or metals such as stainless steel. Temperature is maintained constant by an electric furnace or liquid metal bath. Batch reactors are generally quite large to hold sizeable sample and to minimize surface effects. It is common that a batch reactor has a few hundred milliliters capacity. It is not surprising that given their large size, batch reactors do not meet the ideal laboratory criteria. Temperature is not uniform throughout the reactor and there can be dead volumes within the reactor.

The most difficult problem that the conventional batch reactor faces is that it can only used to study slow reactions whose half-lives  $(t_{1/2})$  are between 15 minutes and 100 hours (Fabuss *et al.*, 1964). For a first order reaction, if the  $t_{1/2}$  is 15 minutes, the reaction rate constant will be  $7.7 \times 10^{-4}$  s<sup>-1</sup>. For the high temperatures used in the current study, the reaction is fast and the heat-up time and cool-down time become non-negligible. However, the batch reactor does have a definite merit over other reactors: the reaction time is accurately known.

Hayashitani (1978) carried out an extensive study of the thermal cracking of Athabasca bitumen using boiling point range criteria and solvent solubility to define pseudocomponents. Many cracking models were proposed that predicted the general experimental trends. A batch reactor with 8 mm OD and 118 mm in length was used and the reaction temperatures were in the range of 300°C to 450°C. Activation energies obtained in all the models were in the range 188 to 293 kJ/mol. Over the temperature range 360 to 422°C, the activation energy for the reaction of middle distillates to light oils was found to be 240 kJ/mol (Model A-3 in the thesis).

#### 2.3.1.2 Curie Point Pyrolysis Reactor

Curie point reactor has a radically different heating and quenching concepts from conventional batch reactors. Even at very high temperature (600 to 800°C), it provides shorter time for feed heat up and product quenching than other types of reactors after a precisely controlled pyrolysis time (Fairburn *et al.*, 1990). This technique was introduced by Simon and Giacobbo (1965).

In Curie point pyrolysis, a thin ferromagnetic wire is coated with a microgram quantity of sample and then placed inside a low volume glass tube. The glass tube is inserted into a high frequency induction coil. The ferromagnetic wire is composed of magnetic nickel-iron-cobalt alloy. When the high frequency field is energized, the ferromagnetic wire is almost instantaneous heated, and hence the sample. 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 and this temperature is then maintained. After a precisely timed interval, an electronically activated hammer mechanism is used to break open the glass microreactor. The pyrolysis products are rapidly quenched by mixing with a stream of cold helium and the product vapors are flushed into a GC/MS system for complete component identification and quantification. Different ferromagnetic alloys have different Curie point temperatures. Therefore, the pyrolysis reaction temperature can be controlled by using different alloy compositions. Wires are available with Curie point temperatures from 300 to 1000°C.

Fairburn *et al.* (1990) studied the kinetics of n-hexadecane pyrolysis using the Curie point pyrolyser. 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. Peak ethylene production (28 wt%) was exhibited at 842°C and 500 ms. Figure 2.1 depicts the results used to determine the activation energy of n-hexadecane pyrolysis, which was determined to be 164 kJ/mol. The desired product of the reaction was ethylene, but olefins up to C15 were obtained in appreciable concentrations under lower conversion (60 to 75%) conditions.

### 2.3.2 Flow Reactors

For reaction times faster than those that can be accurately studied by conventional batch reactors, flow reactors can be used. 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 many commercial pyrolysis units, such as those used for ethane cracking, are large-scale multi-tube reactors.

As with conventional batch reactors, tubular reactors are built with glass or metal tubes. Heat is supplied by the media around the reactor and the reactor wall temperature is



Figure 2.1 Activation Energy Evaluation for n-Hexadecane Pyrolysis (Fairburn et al., 1990)

usually deemed constant. If the gas flow is turbulent, it is assumed that there is no mixing in the direction of flow and complete mixing in the radial direction. This type of reactor is called a plug flow reactor (PFR).

An equivalent reactor volume concept was introduced by Hougen and Watson (1947) to account for slight temperature differences in flow reactors. The equivalent reactor volume is that volume which, at a chosen reference temperature and reference pressure, yields the same conversion as the actual reactor with its temperature and pressure profile. The reference pressure is always one bar and the reference temperature is the average of the process gas temperatures in the last 40% of the reactor. The calculation of the equivalent reactor volume requires an accurate knowledge of the temperature profile along the tube. Strictly speaking, the concept is only valid for a single reaction with a single activation energy or for a set of parallel reactions having identical values of activation energies (van Damme, *et al.*, 1975).

For flow reactors, the key point that requires attention is maintaining the ideality of the PFR operation. In a laboratory, it is difficult to realize plug flow because the Reynolds number is generally less than 100 (Côme, 1983). Therefore, a temperature profile and a velocity profile across the cross section of the tube exist, which means that no single residence time but rather a distribution of residence times exist. At the entrance and exit region, because of the poor heat transfer, reactants may travel a long distance before reaching the reactor wall temperature. To improve the operating conditions, the PFR

tube diameter should be made small to reduce the temperature gradient. The reactor length/diameter ratio should be kept as large as possible so that the effects of thermal entrance and exit regions are negligible.

Gas flow through a tubular reactor experiences a pressure drop along its length. When the reactor tube is long and gas flow rate is high to maintain turbulent conditions, the pressure drop along the reactor may become non-negligible and an equation of momentum conservation is required.

Zhou *et al.* (1987) studied thermal cracking kinetics of several straight-chain alkanes and their mixtures, including C9, C12, C13, C16, and C22. The reactor was a straight tubular reactor under atmospheric pressure and temperature range was 350 to 620 °C. The reactor was 305 mm in length with an inside diameter of 81 mm (a diameter of 81 mm was quoted in the article, however, the diameter is more likely 8.1 mm to give a reasonable length to diameter ratio). For dodecane (C12) thermal cracking, the activation energy was determined to be 164 kJ/mol.

Depeyre *et al.* (1989) studied atmospheric gas oil thermal steam cracking kinetics over a range of 625 to 800°C with the aim of producing olefins, using a helical coil tube reactor at atmospheric pressure. The reactor used was 4 m in length and the inside diameter was 4 mm. A mechanistic radical and molecular model consisted of 138 reactions, 18 species and 24 radicals were proposed. The model made use of a simplified composition

of gas oil. Pure compounds were used to represent each family of hydrocarbons in the gas oil, i.e., n-hexadecane represented paraffins, iso-hexadecane represented iso-paraffins,  $C_{13}H_{26}$  represented naphthenes and  $C_{15}H_{24}$  represented aromatics.

Kumar and Kunzru (1985) studied naphtha pyrolysis over the temperature of 720 to 800°C. An annular tubular reactor was used. The length of the reactor was 60 cm. A model including 21 molecular reactions and an overall reaction of naphtha to gases was reported. The activation energy of the overall reaction for naphtha to gases was found to be 220.8 kJ/mol.

Froment and co-workers conducted a wide range of studies on the thermal cracking of light hydrocarbons and naphtha. They found that the rate of cracking of single hydrocarbons closely followed a first order law (Froment *et al.*, 1976, 1977; van Damme *et al.*, 1975). This is true for naphtha cracking also (van Damme and Froment, 1981). Further, the first-order rate coefficient was shown to be independent of the conversion. In other words, from a kinetic point of view, naphtha cracks as if it were a single component and its disappearance can be described by a conversion. For typical naphtha (boiling point range: 40-195°C), the activation energies were determined to be in the range of 212 to 228 kJ/mol.
## 2.4 The Chemistry of Thermal Cracking

In thermal processes, there are two types of reactions taking place. One, scission, is an endothermic reaction that makes larger molecules break to smaller molecules; the other, called condensation, is an exothermic reaction that converts the smaller molecules to larger molecules. Without catalyst, isomerization reactions or olefin polymerization reactions rarely occur. The generally accepted model for paraffin cracking was first presented 60 years ago and is based on a free-radical mechanism (Kossiakoff and Rice, 1943).

The free-radical mechanism asserts that when a certain molecule undergoes a thermal reaction, it breaks apart first at the position with weakest chemical bond and forms two free radicals. C-C and C-H bond energy data indicate that the reactions most likely take place at C-C bonds of chain paraffins, as well as at side chains of naphthenes and aromatics.

Smaller free radicals such as  $H \cdot$ ,  $CH_3 \cdot$  and  $C_2H_5 \cdot$  may exist for a short time and can consequently collide with other molecules to form new free radicals. However, larger free radicals are very active and are easily broken to form olefins and smaller free radicals. Thus chain reactions occur. When products leave the reaction system, free radicals will combine to form a paraffin and reactions terminate. Therefore, the ultimate products of scission will be paraffins and olefins whose molecular weight is lower than the feed.

This mechanism is illustrated using n-hexadecane thermal cracking as an example (Cheng, 1994). Many free radical reactions are possible for a given reactant; several examples are shown below.

(1) Initiation

Free radicals are formed from the large molecule:

 $C_{16}H_{34} \rightarrow CH_3 \bullet + C_{15}H_{31} \bullet$ 

(2) Propagation

In this stage, a series of reactions occur that converts reactants to products while leaving the concentration of radicals unchanged. The following types of reactions are included:

reactions of radicals with other molecules,

 $CH_3 \bullet + C_{16}H_{34} \rightarrow CH_4 + C_{16}H_{33} \bullet$ 

larger free radicals release H • and form olefins,

 $C_{15}H_{31} \bullet \rightarrow C_{15}H_{30} + H \bullet$ 

$$C_{16}H_{33} \bullet \to C_{16}H_{32} + H \bullet$$

and larger free radicals crack to smaller ones.

$$C_{15}H_{31} \bullet \longrightarrow C_{7}H_{14} + C_{8}H_{17} \bullet$$

$$C_{8}H_{17} \bullet \longrightarrow C_{4}H_{8} + C_{4}H_{9} \bullet$$

$$C_{4}H_{9} \bullet \longrightarrow C_{3}H_{6} + CH_{3} \bullet$$

$$C_{4}H_{9} \bullet \longrightarrow C_{2}H_{4} + C_{2}H_{5} \bullet$$

(3) Termination

Free radicals combine with each other.

$$CH_3 \bullet + H \bullet \longrightarrow CH_4$$
$$C_2H_5 \bullet + CH_3 \bullet \longrightarrow C_3H_8$$

# 2.5 Reaction Kinetics for Complex Mixtures

Petroleum and its upgraded products are very complex hydrocarbon mixtures. Even the lighter fractions such as LGO and naphtha contain a continuous spectrum of hydrocarbons and make the reaction feed and product characterization very difficult. A number of approaches have been applied to deal with complex mixtures. The simplest approach is to treat the reactions as a black box; this approach does not incorporate any chemical insight. Others try to understand the reaction chemistries using model compounds. More recently, Monte Carlo simulations have been used to construct

ensembles of molecules to represent complex mixtures, and then calculate their reaction behaviour. Lumped pseudo components are also applied to represent important classes of compounds with simplified reactions. (Gray, 1997)

# 2.5.1 Black Box Method

This empirical method treats the reaction process as a black box. The following equation is used to determine the extent of reaction in a reactor:

$$\frac{dX}{d(LHSV)} = k(T)X'' \tag{2.1}$$

where X can be a property of the feed, LHSV is the liquid hourly space velocity in the reactor, k(T) is the reaction constant, and n is the order of the reaction. This method has some limitations (Gray, 1997):

- the initial composition is not represented in detail, and therefore, the kinetic constants are unique to a specific feedstock;
- (2) the subsequent reactions of the mixture are not represented in detail, and therefore, it is not suitable to predict performance outside the initial data set;
- (3) this model is reactor-dependent so that it can only be scaled to reactors of similar geometry.

#### 2.5.2 Model Compound Method

In this method, the composition of a complex mixture is first studied in order to select structures of interest and then a model compound is established to represent the feedstock. Then the selected model compound is reacted at the desired conditions. The kinetic study of properly selected model compound can provide insight into the behaviour of more complex or larger molecules.

The main problem that the model compound method faces is that the key interactions between components in the feedstock may be omitted. Another problem is the hypothetical model compounds are sometimes very difficult to obtain.

An important example of using the model compound method is thermal cracking of nhexadecane. n-Hexadecane is a widely chosen model compound (Voge and Good, 1949; Fabuss, *et al.*, 1964; Depeyre and Flicoteaux, 1991; Khorasheh and Gray, 1993).

# 2.5.3 Monte Carlo Simulation Method

This method first uses statistical methods to characterize the structural attributes of a complex hydrocarbon mixture. At least six attributes have been used: paraffin length, number of naphthenic rings, number of side chains, side-chain length, number of aromatic rings and number of naphthenic rings per aromatic molecule (Petti *et al.*, 1994;

Trauth *et al.*, 1994). Then a Monte Carlo method is used to sample these distributions randomly and construct molecules. An ensemble of these molecules represents the heavy hydrocarbon mixture. Finally, each molecule is reacted according to the known behaviour of model compounds and the molecules are collected into appropriate groupings to define the product yield. However, this method is extremely computationally intensive and with the difficulty of modelling different feeds, the method has not yet been used to predict the observable kinetic or product properties (Gray, 1997).

## 2.5.4 Lumped Kinetics

In a mixture with many components, it is often impossible, and almost invariably useless to have a complete description of all components. In fact, industry is often only interested in some sort of lumped concentration.

The lumping method, as introduced by Wei and Kuo (1969) and Kuo and Wei (1969), seeks to represent large monomolecular reaction systems by low-order, linear differential equations involving lumped pseudo-components. These pseudo-components are created by grouping chemical species having similar behaviour. A detailed analysis of lumped-system reaction dynamics was given by Wei and Kuo (1969). Once an appropriate lumping scheme is established, the new lumped-system rate matrix is constructed from the response data (Coxson and Bischoff, 1987a and 1987b).

The kinetic model for fluid catalytic cracking by Jacob *et al.* (1976) is shown in Figure 2.2. Kinetic constants were determined by experiments on sub fractions with controlled composition. The subfractions were resolved in enough detail to have similar reactivity, and therefore, be related to known model compound reactions. The reaction network was then validated by experiments using actual feeds. The model can predict performance even with changes in the feed composition and the operating conditions in the reactor.

One of the limitations of lumped kinetics is that information about individual components, and thus details of the product distribution, is lost. The greatest challenge for applying lumped kinetic methods for a catalytic process is that whenever the underlying catalyst system changes, either from changes in composition or aging, all of the rate constants could change (Weekman, 1979). Fortunately, kinetic studies of a thermal cracking process avoid this disadvantage. Another problem with lumped kinetics is that the structures present in the lumps evolve as the reactions proceed, thus changing the reactivity of the lumps. As a result, the rate constants associated with lumped models are frequently functions of feedstock properties and conversion.



Light Components (220-342°C):

$P_L = paraffins$
$A_L$ = aromatic substituents

 $N_L$  = naphthenes  $C_{AL}$  = aromatic rings

Figure 2.2 Kinetic Model for Fluid Catalytic Cracking (Jacob et al., 1976)

## CHAPTER 3

#### **Experimental Apparatus and Methods**

This section outlines the experimental set-up and the method. Figure 3.1 is a photograph of the experimental apparatus. Figure 3.2 is a simplified schematic diagram of the apparatus, while a detailed diagram is shown in Figure 3.3. Solid black valves are always closed in the current study and the main process flow is shown by a thicker line. Figure 3.4 is a detailed diagram of the condensing and product collection systems.

## 3.1 **Process Overview**

A helical coil reactor was used for the light gas oil thermal cracking kinetic study. Pumps pushed the hydraulic oil (HO) and therefore moved the piston of a transfer cylinder to force the hydrotreated light gas oil (LGO) feed into the preheaters. After the feed oil was preheated to about 350°C, it was combined with 350°C nitrogen coming from the furnace. Nitrogen was used to dilute the reactant oil and its flow rate was adjusted to achieve different gas oil residence times in the reactor. Once inside the reactor, feed gas oil was rapidly heated to reactor temperature. Reynolds number was found to be about 2500 and the temperature rose at a rate of approximately 800 K/m (see Appendix E for detailed calculations). At the exit of the reactor, products were quenched in a series of three water-cooled condensers (Figure 3.4). A portion of the reactor outlet fluid was trapped after each condenser in a flask submerged in an ice bath.



Figure 3.1 Picture of LGO Thermal Cracking Experimental Set-up



Figure 3.2 Simplified Schematic Diagram of LGO Thermal Cracking Apparatus



Figure 3.3 Helical Coil Reactor Process Flow Diagram

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A demister full of rayon fibre (fibre made by Kendall Canada Inc.) absorbed the uncondensed aerosol before gas products entered a wet test meter (WTM).

The volume of gaseous products was measured by a wet test meter, and gases were collected in a 200-litre gas bag. After the feed was stopped, nitrogen continued to flow through reactor to sweep the remaining hydrocarbons to the reaction gas bag. Coke make was evaluated using a burn procedure once the reactor had been well purged. Another gas bag was employed for the gas product from the coke burn procedure.

The liquid product was collected from the flasks. Flasks, condensers and pipes were cleaned completely using dichloromethane (Anachemia Canada Inc., > 99.5% purity). Product oil was then separated from the dichloromethane by a small laboratory distillation unit inside a fume hood.

# 3.2 Experimental Apparatus

## 3.2.1 Helical Coil Reactor

The reactor coil is a total of 18 m in length. It is comprised of two pieces of stainless steel tubes welded together. The inside diameter (ID) of the first 9 m was 3.34 mm (3/16" tubing), while the second half of the reactor had a larger ID of 6.16 mm (5/16" tubing) to accommodate the increased volume of cracked gases. The two parts were

welded together. As shown in Figure 3.5, the helical coil was wound into a groove around a 10cm diameter stainless steel bar stock. Detailed dimensions of the reactor are shown in Figure 3.6. This assembly was contained within a larger cylindrical section of bar stock (see the lower section of Figure 3.5). Reactor length is long enough (length/diameter > 1000) to eliminate the effects of entrance and exit region. The long reactor tube was coiled to allow it to fit in a smaller bar stock.

The bar stock was heated both from the centre and the exterior. The large thermal mass provided energy for the endothermic reactions. Figure 3.7 shows the arrangement of reactor heaters. Heaters are made by ARI Industries, Inc. Two heaters were coiled around the larger cylindrical section of bar stock holding the reactor assembly. They had a heated length of 3.20 m, 6.4 mm in diameter, 7200 W power and  $1.132 \times 10^5$  W/m<sup>2</sup> power density at 230 volts. A third smaller heater made by ARI was used to heat the bottom section only. This heater accounts for convection effects. Six others were installed at the centre of the reactor assembly.

## 3.2.2 Transfer Cylinder and Hydraulic System

As shown in Figure 3.3, the hydraulic system comprised a hydraulic oil reservoir, an overflow tank, hydraulic oil filter, flowmeters and three pumps.



Figure 3.5 Photograph of the reactor



Figure 3.6 Detailed Dimensions of the Reactor



Figure 3.7 Arrangement of Reactor Heaters (Outside)

The two pumps (pump #2 and #3 in Figure 3.3) used in the current study were made by Milton Roy Company (product number 9-2015003). They are displacement type and can raise pressure up to 40 MPa. Both pumps operating together can generate a maximum flow rate of 0.3 g/s of LGO. A hydraulic oil filter was installed before the pumps to remove the possible particles or debris. As shown in Figure 3.3, pressure safety valves were used to protect the rest of the system from overpressure. They were set at 0.5 MPa. The pump had a knob with scale ranging from 0 to 100. These two pumps were set in parallel and the calibration was done with both pumps on and at the same setting on the scale. The calibration curve for the LGO flow rate is given in Appendix C. A photograph of the two pumps is shown in Figure 3.8.

A transfer cylinder bridged the hydraulic system and the LGO feed. A photograph of the transfer cylinder can be found in Figure 3.9. Pumps pushed the hydraulic oil to move the piston in the transfer cylinder. The volume of the transfer cylinder was 2.3 litres and the piston diameter was 10 cm.

As shown in Figure 3.3, Hydraulic oil was stored in a reservoir. By opening valves H1, H5, H9, H10, H11, H12 and closing valve F4T, hydraulic oil was able to circulate within a closed circuit. Once valve H12 was turned off and valve F4T was turned on, pumps could push hydraulic oil to move the piston in the transfer cylinder.



Figure 3.8 Pumps (#2 and #3), Furnace and Hydraulic Oil Flow Meter



Figure 3.9 Transfer Cylinder and Pumps (#2 and #3)

#### 3.2.3 Feed Preheaters and Gas Furnace

Feed LGO was heated from room temperature to about 350°C by two preheaters. Before nitrogen was mixed with the preheated feed LGO, it was heated to 350°C by a furnace. The furnace was also employed to preheat air to 350°C before it entered the reactor during coke burning.

The furnace was a Series 3110 tube type furnace made by Applied Test Systems Inc. The maximum operating temperature was  $1010^{\circ}$ C and the power was 1,332 W. It had single-zone construction and the heated length was 0.71 m. The dimensions of the furnace were 9.5 cm ID × 79 cm length. A photograph of the furnace can be found in Figure 3.8.

# 3.2.4 Product Condenser and Collection

The reaction effluent was quenched, and then further cooled in a series of water-cooled condensers. The first condenser had a 40 cm long copper water jacket outside a stainless steel tube and the other two condensers were regular glassware condensers 30 cm in length. As shown in Figure 3.4, after each condenser, there was a flask to collect the condensed products. Cold water flowed through the shell side of each condenser. Each flask was placed in an ice bath. A demister full of rayon was installed after the

condensers to coalesce any aerosol before gas products entered a wet test meter. A photograph of the condensing system and demister is shown in Figure 3.10.

As shown in Figure 3.2, the volume of the gaseous reaction product combined with nitrogen was measured by a WTM (DM3C-2.5; G. H. Zeal Ltd.; drum capacity 2.5 litres). The gas was then collected in a gas bag. The gas bag had a capacity of 200 litres. Coke burning product was also measured by the WTM and collected using another bag with the same capacity. A photograph of the WTM and gas bag can be seen in Figure 3.1.

After each run, the condensers, flasks, demister and pipes connecting them had to be completely cleaned using dichloromethane (normal boiling point is 40°C). Dichloromethane and oil product was separated in a simple batch laboratory distillation unit. A photograph of this unit is shown in Figure 3.11.

## 3.2.5 Process Instrumentation and Data Acquisition

All the thermocouples used in the current study were calibrated K type made by Alltemp Sensors. They were installed at the preheaters, furnace and reactor. Temperatures at the reactor inlet and outlet were measured by thermocouples in the fluid. The inlet thermocouple was 1.6 mm (1/16 inch) in diameter and was placed about 30 cm into the reactor tube. The inlet thermocouple may actually be touching the reactor tube wall.



Figure 3.10 Picture of Condensing System



Figure 3.11 Picture of Distillation Unit

However, because of the rapid heat transfer (see Appendix E for detailed calculations), the wall and fluid temperature equalizes within approximately 20 cm. The outlet thermocouple was 1.6 mm (1/16 inch) in diameter and was inserted into a T-connection about 10 cm away from the reactor bar stock. The T-connection was covered by a 10 cm thick insulation to minimize heat losses. Because of the T-connection, the outlet thermocouple was measuring the fluid temperature.

Temperature control was realized by UT350 general-purpose controllers for the reactor, preheaters and furnace. The controllers were made by Yokogawa Electric Corporation with an input sampling cycle of 250 ms, an input accuracy of  $\pm 0.1\%$  of full scale for process variables and an output accuracy of  $\pm 0.3\%$  of the span. The controllers can be operated in "Auto" or "Manual" mode. Prior to an experiment during the heat up stage, a certain percentage of power was set and once the temperature was close to the set point, it was then switched to Auto control mode. LabView (Version 4.1) with a pentium computer was used as an on-line temperature data acquisition device. The reactor inlet and outlet temperature were measured and stored in a file every two seconds.

# 3.3 Light Gas Oil Properties

Hydrotreated light gas oil, used as feed in the current study was provided by Syncrude Canada Ltd. Some properties of the hydrotreated LGO are given in Table 3.1.

	hydrotreated light gas oil	
Density at 15°C, g/ml	0.878*	
SimDist <sup>+</sup>		
5% off, °C	180	
10% off, °C	210	
90% off, °C	370	
95% off, °C	400	
Mean MW, g/mol	212	
(estimated from SimDist)		

Table 3.1 Properties of Feed Light Gas Oil

\*(Yui, 1999)

<sup>+</sup> (Table A.1)

#### 3.4 Gases Used in the Study

Nitrogen used in LGO thermal cracking experiments, air used in the coke burning procedure, and helium used in GC analysis were all produced by Praxair. Table 3.2 gives the product grades and quality specifications of the gases used in this study. Air used in the coke burning procedure was tested for  $CO_2$  and CO content on the GC; only trace quantities were found. Therefore, coke analysis will not be affected.

# 3.5 Light Gas Oil Thermal Cracking Experiments Procedure

The light gas oil thermal cracking experiments were conducted using a procedure developed in this study. The steps outlined below were strictly followed in the given order for all experiments in this study. A detailed process flow diagram of the apparatus is shown in Figure 3.3. Solid black valves are always closed in the current study.

Prior to an experiment, condensers were disassembled and meticulously cleaned including the product collecting flasks, demister and process piping. The last one of three liquid product-collecting flasks (refer to Figure 3.4) and the rayon for the demister were weighed. WTM water level was checked and adjusted as instructed in the WTM manual. The transfer cylinder was detached and checked to find out how much feed was left, refilled as necessary and then reinstalled. Rayon was evenly put into the demister. It was very important that the demister should be assembled upside down so that the

	Nitrogen	Air	Helium
Product Grade	Oxygen Free	Hydrocarbon Free	5.0 UHP
O <sub>2</sub>	< 0.5 ppmv	19.5 – 23.5%	< 1 ppmv
N <sub>2</sub>	99.998%	-	< 5 ppmv
Helium, %	-	-	99.999*
H <sub>2</sub> O	-	< 3 ppmv	<2 ppmv
тнс	-	< 0.1 ppmv	< 0.5 ppmv
H <sub>2</sub>	-	-	< 1 ppmv
CO <sub>2</sub>	-	< 0.1 ppmv	< 1 ppmv
со	-	<0.1 ppmv	< 1 ppmv

# Table 3.2 Product Specification of Gases Used in Experiments

\* Neon free basis.

rayon could be packed more tightly at the entrance and exit. Finally, the demister, condensers and flasks were reassembled. SS-30 copper anti-seize compound (Jet-Lube of Canada Ltd.) was used to thoroughly coat the fitting between the first condenser and the reactor. Vacuum grease was put onto the joints of all glass condensers and flasks. The gas bags were marked and always used for the same purpose. Gas bags for reaction and coke burning were vacuumed using the building vacuum line, refilled with nitrogen and then vacuumed again. This should effectively get rid of the potentially remaining hydrocarbons or  $CO_2$  and CO. The reaction gas bag was then attached to the apparatus.

The valves and piping were checked and then nitrogen was introduced at a small flow rate of about eight ml/s before raising the reactor temperature. LabView software was then loaded and a data file was created to monitor and record the temperatures. The reactor heaters power were set to 20% and furnace power to 25% using the temperature controllers on the control board. The cooling water flow to the condensers was started at this time and the exhaust gas was allowed to flow to the wet test meter.

The reactor required four to five hours to reach its final operating temperature. Although the temperature controllers could be used to adjust power in the "Auto" mode to stabilize at the desired set point, there was oscillation within a range of 10°C and a period of approximately 40 minutes. Experience showed that at 4-6% power, after the reactor reached the set point, could maintain the reactor temperature constant for at least 2 hours. Manual power settings were therefore used for experiments. Preheaters were then turned on with 20% power; it took them about 2 hours to reach 350°C. Once the preheaters reached the set points, they were set to "Auto" mode.

Half an hour before the reactor reached its desired temperature, the oil feed pumps #2 and #3 were started in order to circulate hydraulic oil within a closed loop and stabilize pump operation. Special attention should be paid to the low flow rate operation. A large flow rate should be used, and then reduced to desired flow rate. This ensured there was flow going through the pumps. These pumps needed 20 minutes to be stabilized.

Ice was added to containers surrounding the flasks. Current atmospheric pressure was recorded from a barometer. Nitrogen flow rate was increased to the desired value by measuring flow volume going through the WTM within a known time period. Valve P6 in Figure 3.3 was opened to stop the flow going through the WTM so that it could be zeroed.

Valve F6 was opened to prepare to bleed the feed oil to a waste oil tank. Immediately after valve F4T was opened, valve H5 was closed to stop hydraulic oil circulating and start to feed preheaters. Feed oil thus went through both preheaters and exited from valve F6 to the waste oil tank (a 4 litre metal can). After about two minutes, the feed flow coming from F6 becomes stable. While waiting for a stable feed flow, nitrogen flow was directed to the gas bag (close P6, P7 and open P8).

The experiment started when valve F6 was closed and F7 was simultaneously opened to feed the reactor with light gas oil. An assistant operator started the timer to record the feed time.

After about 15 to 30 minutes of run time, valve F7 was closed and the bleed valve F6 was simultaneously opened. The timer was stopped and feed time recorded by the assistant operator. Valve F6 was closed after pumps were turned off. Nitrogen flow through the reactor was continued until condensers became clear. During nitrogen purging, the gas chromatograph (GC) was prepared for analysis of the gas samples. To stop the flow of nitrogen to the gas bag and switch it to the vent, valves P6 and P7 were opened and P8 was closed simultaneously. One should take care not to overpressure the WTM during this operation. Reaction gas volume was read from WTM. Data acquisition with LabView was stopped and data saved.

A Hamilton SAMPLELOCK syringe was used to obtain a 10 ml gas sample from the reaction gas bag, which was analyzed by GC.

Before burning, the reactor temperature was raised to 600°C and coke-burning gas bag was attached to the system. LabView was started for monitoring purposes only. Ice was added into bucket with cooling coil for coke burning. Valve P4 was then opened. The first condenser (shown in Figure 3.4) was detached from the system and the rest of the condensers were isolated. Before the cooler for coke burning was attached to the reactor, anti-seize compound should be thoroughly coated to its fitting.

After the WTM was zeroed again, valve P8 was opened and valves P6 and P7 were closed to direct nitrogen into the gas bag. Air was then introduced by closing valve F10 and opening valves F11 and F12. Coke burning continued for about one hour. Then air flow was directed to vent. Total gas bag volume was recorded by the WTM. The Hamilton SAMPLELOCK syringe was also used to obtain this gas sample for GC analysis.

After the run, the condensers were again disassembled and completely cleaned with dichloromethane. Liquid product was first mixed and collected in the flask immediately before the demister, and then the flask was weighed. After weighing, the liquid product was collected in sample bottles for future analysis. The mixture of oil and dichloromethane was then distilled to remove dichloromethane and residue was weighed. Rayon in the demister was also weighed.

## 3.6 Product Analysis

Product analysis included GC analysis of gaseous products and simulated distillation analysis of the reaction liquid product. Because the coke make was very small, no attempt was made to analyze the coke properties.

#### 3.6.1 Gas Analysis

In the current study, a Hewlett-Packard (HP) 6890 gas chromatograph (GC) and HP ChemStation software have been employed. The GC has a large column oven, dual injection ports and a thermal conductivity detector (TCD). The HP ChemStation software contains all parameters for instrument control, data acquisition and evaluation, including integration, quantification and reporting.

Two columns were employed: HP – Plot Molecular Sieve (MS) 5A, 15 m × 0.53 mm × 50.0  $\mu$ m film thickness and HP – Plot Q, (Divinylbenzene/styrene Porous Polymer), 30 m × 0.53 mm × 40.0  $\mu$ m film thickness. These fused silica capillary columns provide a quicker analysis time with better resolution than the traditional packed columns. However, these columns should not be exposed to temperatures greater than 250°C. Thus, the maximum GC oven temperature was 250°C. The MS column was used to separate inerts (O<sub>2</sub> and N<sub>2</sub>), methane and carbon monoxide. The Plot Q column separated carbon dioxide, ethane and heavier hydrocarbons.

An analytical method was set up to analyze the reaction gas bag and coke burning bag. This method was a collection of set points required to run a single gas sample on the GC. Table 3.3 summarizes the operating conditions used in gas sample analysis. Details on the GC method can be found in Appendix D.

Reference Flow	Helium, 22 ml/min	
Temperature Program	Initial temperature 60°C	
	0-2 min, 60°C	
	2-4 min, ramp to 80°C at 10°C/min	
	4-9.7 min, ramp to 250°C at 30°C/min	
Total Analysis Time	9.7 min	
System Temperature:		
Inlet	140°C	
TCD	260°C	
TCD Detector:		
Range	0.025 mV full scale	
Data Range	20 Hz	
Minimum Peak Width	0.01 min	
Cylinder Pressures		
Helium	620 kPa gauge (90 psig)	
Air	480 kPa gauge (70 psig)	

Table 3.3 Gas Chromatograph Analysis Conditions

## **3.6.1.1 GC Calibration**

Calibration is the process of determining response factors used to calculate absolute component concentrations by injecting specially prepared calibration samples. The calibration table is also used for peak identification.

Single-level calibration method was used for hydrocarbons and  $CO_2$  was calibrated using a multi-level method. The response of the detector is assumed linear over the working range of concentrations for the samples of interest. The response factor for a given component peak is given by the inverse of the slope of the calibration curve line through the point and the origin.

A calibration sample, also referred to as a calibration standard or a standard mixture, is a sample containing a known amount of the compound to quantify. Figure 3.12 shows a chromatograph of the standard gas mixture and its composition is shown in Table 3.4.

# 3.6.2 Simulated Distillation Analysis of Liquid Samples

Simulated distillation methods are chromatographic techniques which provide data that emulates glassware distillation through gas chromatography. ASTM method D2887 was used for the current study. The column (Series Number 289215) is 10 m  $\times$  0.9 micron film thickness and 0.53 mm ID. The external standard is ASTM D2887 reference gas




۶S

Component	mol %	Component	mol %
O <sub>2</sub>	1.5	i-C₄H10	0.5
СО	10	n-C₄H10	0.5
CH₄	5	i-C <sub>5</sub> H <sub>12</sub>	0.5
C <sub>2</sub> H <sub>6</sub>	5	n-C5H12	0.25
C <sub>2</sub> H <sub>4</sub>	2	i-C <sub>6</sub> H <sub>14</sub>	0.25
CO <sub>2</sub>	20	n-C6H14	0.25
C <sub>3</sub> H <sub>8</sub>	2	N <sub>2</sub>	50.25
C3H6	2		

 Table 3.4
 Standard Gas Mixture Composition for GC Calibration

oil, and the retention time standard is SD-SS3E-05 (carbon number ranges from C4 to C66). The column and the standards are made by Separation Systems Inc.

#### **CHAPTER 4**

#### **Results and Discussion**

In keeping with the objectives of this study, hydrotreated Light Gas Oil (LGO) has been pyrolysed at temperatures varying from 500 to 550°C. Because of the complexity of the reaction system, a number of runs with and without LGO feed were performed in order to identify and debug various operating problems with the reactor, condenser, demister, pumps, instrumentation and other equipment. The results of these studies prompted many design additions and modifications, such as using different condensers, a demister and a gas bag, as well as using the two pumps providing the smallest flow rate. Besides those tests, eight successful runs were conducted where light gas oil was fed to the reactor. A summary of all successful experiments appears in Table 4.1. Reactor temperature profiles are given in Appendix B. The feed time shown in Table 4.1 is the interval between the feed starting and feed stopping (see Figure B.1). A summary of the operating conditions used in each of the successful experiments is shown in Table 4.2. Unsuccessful experiments are listed in Appendix H.

A simple four-lump kinetic model for the LGO thermal cracking reaction was developed and kinetic parameters are calculated and discussed. The simple model allows us to determine the amount and rate at which the LGO pseudo-component is converted to the desired product (naphtha) and to by-products (gas and coke).

# Table 4.1 Summary of Successful Experiments

Run	Date	Reactor	Feed Time,	Comments
		Temperature, °C	S	
1	99-08-31	550	1256	First successful run at 550°C.
2	99-11-09	530	1212	Successful run at 530°C.
3	99-11-17	500	1596	Longest pyrolysis experiment performed in study. Over 200g of LGO processed.
4	99-12-01	550	1584	Successful repeated run.
5	99-12-15	500	1386	Successful repeated run.
6	00-02-02	550	836	Successful repeated run.
7	00-03-27	550	779	Successful run with higher feed flow rate.
8	00-04-03	530	912	Successful run with higher N <sub>2</sub> flow rate.

Run	T, ℃	Feed Flow	N <sub>2</sub> Flow	LGO/N <sub>2</sub>	Residence Time
		Rate (g/s)	Rate (L/s)	mass ratio	(s)
3	500	0.1314	0.058	2.0	1.73
5	500	0.1314	0.058	2.0	1.73
2	530	0.1314	0.058	2.0	1.64
8	530	0.1314	0.075	1.5	1.35
1	550	0.1314	0.058	2.0	1.58
4	550	0.1314	0.058	2.0	1.58
6	550	0.1314	0.058	2.0	1.56
7	550	0.1838	0.058	2.7	1.41

Table 4.2 Summary of Experimental Conditions

## 4.1 Material Balance

Products from each run included the gas in reaction gas bag, coke in the form of  $CO_2$  in the burn gas bag, liquid product directly collected from the flasks after each condenser, liquid product recovered from remaining oil in the condensers and pipes, and liquid product in the form of mist trapped by cotton in the demister. Table 4.3 gives a summary of the mass balances. More details on the material balance can be found in Appendix A.

## 4.2 Product Analysis

As outlined in Chapter 3, the reaction gas products were analysed by an HP6890 TCD gas chromatography. The liquid products were analysed by an HP6890 simulated distillation system.

## 4.2.1 TCD GC for Gas Product Analysis

An HP6890 TCD GC was employed to analyse gas in the gas bags after each run. Example chromatograms of the reaction gas product and the coke burning gas product are shown in Figures 4.1 and 4.2. Although a GC equipped with a flame ionization detector would be more accurate, the potential error in overall mass balance was small

Run	Т	Feed	L	G	С	Recovery	L	G
	(°C)	(g)	(g)	(g)	(g)	wt% of	wt% of	wt% of
						feed	product	product
3	500	209.7	188.1	12.7	0.05	95.8	93.6	6.4
5	500	182.0	164.4	10.3	0.05	96.0	94.1	5.9
2	530	159.2	130.9	20.3	0.20	95.1	86.6	13.4
8	530	119.8	97.7	14.3	0.10	93.6	87.2	12.8
1	550	165.0	118.8	40.5	0.35	96.8	74.6	25.4
4	550	208.2	147.4	52.0	0.40	96.0	73.9	26.1
6	550	109.9	75.4	29.0	0.30	95.3	72.2	27.8
7	550	143.2	103.6	34.4	0.30	96.6	75.1	24.9

Table 4.3 Summary of Mass Balances



Figure 4.1 Chromatograph of Reaction Gas Product of Run #7





since the mass of the heavier components (C5+) for which the TCD would be less accurate formed only a small percentage of the total gaseous product.

#### 4.2.2 Liquid Sample Analysis

Resolution of mixtures by gas chromatography is limited to hydrocarbons up to 12 carbons (molar mass of 170). Beyond this size, the numerous isomers are too similar in their properties to be separated by a chromatographic column. Mass spectrometry can provide information on homologous series up to a molar mass of 1500, after extensive preparative separation of the samples. However, the currently available GC/MS device could not resolve the light gas oil feed and its thermal cracking products because of the large number of isomers. PONA (Paraffins, Olefins, Naphthenes and Aromatics) analysis was considered in the study. However, with currently available devices, a satisfactory PONA analysis was not possible because the column was not long enough (40 m) and could not separate the peaks effectively. NMR analysis is useful for characterizing the average molecular characteristics, but it cannot give boiling distributions of species (Gray et al., 1991; Ternan et al., 1994). Consequently, the mixture of components in the feed and the products defy any attempt at complete component-by-component analysis. Therefore, simulated distillation (SimDist) is the best alternative for the liquid analysis.

As explained previously, the liquid products collected were analyzed by simulated distillation gas chromatography (SimDist) according to ASTM method D2887-89. From the results of SimDist, it is found that the boiling point range and end boiling point have been reduced significantly after the feed light gas oil was thermal cracked. The higher the reaction temperature, the lighter the product. Simulated distillation curves for feed and products at three different reaction temperatures are shown in Figure 4.3. SimDist results for all eight experiments are shown in Appendix A.

No attempt was made to mix the light condensate collected in the demister with the product oil prior to the liquids analysis. However, the oil trapped by the demister was considered part of the naphtha component because after the second condenser the stream temperature had already dropped to room temperature and the demister was located after the third condenser.

## 4.3 Residence Time

The residence times were calculated by assuming the molecular weight of the fluid in the reactor is the average value of the inlet feed and outlet stream. Gases in the reactor were at low pressure (slightly above atmospheric pressure) and high temperature (500-550°C), so the compressibility factor is equal to one and the gases can be assumed to behave ideally. The molecular weights of feed and liquid products were estimated by the results of the simulated distillation (SimDist) analysis. The molecular weight of gas



Figure 4.3 Simulated Distillation Curves for Feed and Products

product was calculated from the gas chromatograph results. (See Appendix A for details of the calculations.)

$$t = \frac{V}{v} \tag{4.1}$$

$$v = \frac{\dot{m}RT}{P\overline{M}} + \frac{v_{N2}T}{T_0}$$
(4.2)

where:

<i>m</i>	feed mass flow rate, g/s
$\overline{M}$	average molecular weight of inlet feed and outlet product, g/mol
Р	reaction pressure, Pa
R	gas constant, J/mol K
t	residence time, s
Т	reaction temperature, K
To	room temperature, 296 K
ν	volumetric flow rate at reactor conditions, m <sup>3</sup> /s
v <sub>N2</sub>	nitrogen volumetric flow rate at room temperature, m <sup>3</sup> /s
v	reactor volume, m <sup>3</sup>

## 4.4 Kinetic Model Development

## 4.4.1 Lumped Reaction Network

Lumped pseudo components were applied to represent classes of compounds with simplified reactions (for example, Wei and Kuo, 1969; Jacob *et al.*, 1976; Weekman, 1979). A set of four lumps divided by boiling point range is suggested. The four lumps in the reaction system include naphtha (boiling point less than 196°C), light gas oil (boiling point greater than 196°C), gas (n-butane and lighter components) and coke. According to these categories, C5 and C6 in the reaction gas bag and the mist trapped by the demister are included in the naphtha boiling range.

A four-lump cracking reaction scheme was chosen to represent the cracking reactions taking place in the reactor because of its simplicity and its ability to predict the product distribution. Figure 4.4 shows the four-lump reaction network.

There was a large volumetric expansion in the helical coil reactor due to the cracking reactions. In order to be consistent and to be realistic, in this study all reaction rate calculations were performed on a mass basis.



Figure 4.4 Kinetic Model for LGO Thermal Cracking

(numbers in brackets are pseudo-components)

## 4.4.2 Model Assumptions

According to this scheme, gas oil cracks to form naphtha, gas and condenses to coke while naphtha may crack further to form gases. It is assumed that the coke formed by condensation reactions from the naphtha fraction is negligible compared to coke formed from gas oil cracking. It is believed that the activation energy of gas producing coke is much higher. Therefore, the coke formation reaction rate is very low and it is reasonable to assume that gas will not condense to form coke at the temperature range of interest.

In thermal cracking studies, nitrogen or steam has been employed as a diluent in tubularflow reactors in order to control hydrocarbon partial pressure and residence time (Depeyre *et al.*, 1989; Khorasheh and Gray, 1993). These inert gases can reasonably be assumed to have no direct effect on the homogeneous thermal cracking reactions if the reactions are approximately first order and if the reaction rate constants are independent of feed concentration. Steam, however, may have an indirect effect on the reactions by reacting with coke via the following reaction.

$$C (Coke) + H_2O (Steam) \longrightarrow CO + H_2$$
 (4.3)

Steam also contributes the formation of metal oxides on the reactor surface. The steam treatment of temperature-resistant Incoloy 800 at 800°C for 24 hours resulted in significant formation of NiO, Fe<sub>3</sub>O<sub>4</sub> and hydrogen. (Tsai and Albright, 1976)

$$(metal)_{surface} + H_2O \longrightarrow (metal oxides)_{surface} + H_2 \qquad (4.4)$$

Because steam was not employed in the study, it is unlikely that surface effects played a major role.

At least seven surface reactions are thought to occur during most industrial pyrolysis. In a complex while not completely understood manner, they all contribute directly or indirectly to coke formation. Coke formation is undesirable in general because it decreases yields of desired products and increases heat transfer resistance. If there were significant coke formation in our study, it could also increase reactor tube pressure drop. For the hydrotreated light gas oil feed at the reaction temperature range of this study, it has been found that the coke formation reaction rate is very small compared to that of other cracking reactions. Therefore, reactor wall surface effect can be assumed to be negligible.

As indicated by Kays and Crawford (1993), the effect of including the hydraulic and thermal entrance regions on the tube temperature profile is small for length/diameter ratios greater than 50. Thus, the entrance regions are neglected because of their minor effect in the long reactor tube used in this project (length/diameter >1000). At reactor temperatures of 500 to 550°C, light gas oil is vaporized essentially instantaneously (99% vaporized at 470°C; see Figure 4.3). Reynolds numbers for the experiments ranged from 2500 to 3000. These are in an acceptable range of turbulent flow to ensure plug flow

operation and rapid heat transfer for LGO heating up and quenching (see Appendix E for detailed calculations of heat up rate and Reynolds number). Detailed calculations for pressure drop are included in Appendix F.

## 4.4.3 Evaluation of Pseudo-Component Fractions

As explained previously, the four pseudo-components are naphtha, gas oil, gas and coke. The mass of gas pseudo-component was calculated using methane to n-butane concentrations from the GC analysis results of the reaction gas bag and the gas bag volume from the WTM. The mass of gas is calculated as follows.

$$m_{gas} = \frac{PV_{gasbag}}{RT_{g}} \sum \left(\frac{M_{i}Y_{i}}{100}\right)$$
(4.5)

Assuming the C/H mole ratio to be 1:1, using  $CO_2$  concentration obtained from GC analysis results of the coke burning gas bag and the gas bag volume from WTM, the mass of coke pseudo-component was calculated as follows:

$$m_{coke} = 13g / mol \frac{PV_{gasbag}}{RT_o} \frac{Y_{CO_1}}{100}$$
(4.6)

With the result of liquid product SimDist analysis, concentration of C5+ from GC analysis results of the reaction gas bag and the weight increase of the demister, the mass of naphtha pseudo-component can be calculated as following:

$$m_{naphtha} = m_{demister} + (m_{liquid} - m_{demister}) \times y_{gasoil} + m_{C5+}$$
(4.7)

 $m_{liquid}$  is the mass of total liquid product trapped in the demister and the three condensers.

The gas oil pseudo-component is simply the heavier portion (SimDist > 196°C) of the liquid product (exclusive demister weight increase).

$$m_{gasoil} = \left(m_{liquid} - m_{demister}\right) \times y_{gasoil}$$
(4.8)

Therefore, the weight percent of each pseudo-component in the total experimental products can be obtained and is shown in Table 4.4. Conversions of LGO pseudo-component are also listed in Table 4.4.

## 4.4.4 Reaction Network Equations and Rate Constants

The reactor was assumed a plug flow reactor. By considering a small volume of reactants flowing through the reactor tube, the kinetic equations of the plug flow reactor

Run	Τ,	Naphtha	LGO	Gas	Coke	LGO Mass
	°C	x1, wt%	x <sub>2</sub> , wt%	x3, wt%	x4, wt%	Conversion, %
Feed	-	6	94	0	0	-
3	500	15.16	78.69	6.12	0.02	16.3
5	500	13.69	80.61	5.67	0.03	14.2
2	530	22.99	64.13	12.75	0.13	31.8
8	530	22.31	66.19	11.42	0.09	29.6
1	550	23.54	52.13	24.12	0.22	44.5
4	550	24.84	50.44	24.52	0.20	46.3
6	550	26.10	48.78	24.83	0.29	48.1
7	550	26.97	50.76	22.05	0.22	46.0

 Table 4.4
 LGO Conversion and Pseudo-Component Distribution

and those of the batch reactor are essentially the same as long as the volume is constant. For thermal cracking reactions, volume expansion is significant (about 3 times under the conditions in this study). However, the batch reaction equations may still be used on a mass basis. According to the reaction network shown in Figure 4.4, first order reaction kinetic equations for the four reactions are outlined below. The reaction network results in a system of four ordinary differential equations, which must be integrated.

$$\frac{dx_1}{dt} = k_1 x_2 - k_2 x_1 \tag{4.9}$$

$$\frac{dx_2}{dt} = -(k_1 + k_3 + k_4)x_2 \tag{4.10}$$

$$\frac{dx_3}{dt} = k_2 x_1 + k_3 x_2 \tag{4.11}$$

$$\frac{dx_4}{dt} = k_4 x_2 \tag{4.12}$$

The integrated form of equations (4.9) to (4.12), become:

$$x_{1} = x_{10}e^{-k_{2}t} + \frac{k_{1}}{k_{2} - k}x_{20}\left(e^{-kt} - e^{-k_{2}t}\right)$$
(4.13)

$$x_2 = x_{20}e^{-kt} (4.14)$$

$$x_3 = 100 - x_1 - x_2 - x_4 \tag{4.15}$$

$$x_4 = \frac{k_4}{k} x_{20} \left( 1 - e^{-kt} \right) \tag{4.16}$$

$$k = k_1 + k_3 + k_4 \tag{4.17}$$

where:

k1, k2, k3, k4	first order rate constants for reactions 1, 2, 3, 4, $s^{-1}$
t	residence time, s
x <sub>10</sub> , x <sub>20</sub>	initial (feed) weight percent of pseudo components 1 (naphtha)
	and 2 (LGO)
x <sub>1</sub> , x <sub>2</sub> , x <sub>3</sub> , x <sub>4</sub>	weight percent of pseudo-component 1 (naphtha), 2 (LGO),
	3 (gas), 4 (coke)

 $x_{10}$  and  $x_{20}$  are known from the SimDist analysis of the feed,  $x_1$ ,  $x_2$ ,  $x_3$  and  $x_4$  are determined from the experimental material balances, and the residence time is calculated assuming an average molecular weight and ideal gas flow.

Based on Equations (4.13) to (4.17), a non-linear regression method was used to determine the reaction rate constants at different reaction temperatures. The reaction rate constants,  $k_1$  to  $k_4$ , were calculated using the Microsoft EXCEL 2000 solver function. Although more than one result could be obtained, only one set was reasonable for a particular run. Negative results were rejected due to physical constraints and the order of magnitude of reaction rates was compared to literature on thermal cracking. The initial estimate supplied to the solver function could be changed by 30 percent without affecting the converged results. The results are shown in Table 4.5. A set of detailed tables for the calculation of average molecular weight of feed and products, feed and product component weight percent and residence time can be found in Appendix A.

## 4.4.5 Frequency Factors and Activation Energies for the Four-Lump Model

Once the reaction rate constants at different reaction temperatures have been determined, activation energies and frequency factors can be calculated by the Arrhenius relationship:

$$\ln k_j = -\frac{E_j}{RT} + \ln A_j \tag{4.18}$$

where:

 $A_j$  frequency factor for reaction j, s<sup>-1</sup>

Run	Temperature, °C	1000×k <sub>1</sub> , s <sup>-i</sup>	1000×k <sub>2</sub> , s <sup>-1</sup>	1000×k <sub>3</sub> , s <sup>-1</sup>	1000×k4, s <sup>-1</sup>
3	500	71	75	32	0.17
5	500	60	77	29	0.19
2	530	184	254	48	1.03
8	530	205	272	54	0.84
1	550	300	580	70	1.95
4	550	330	599	61	1.81
6	550	347	569	69	2.66
7	550	369	561	65	2.19

 Table 4.5
 LGO Thermal Cracking Reaction Rate Constants

- E<sub>j</sub> activation energy for reaction j, J/mol
- $k_j$  first order rate constant for reaction j, s<sup>-1</sup>
- R gas constant, 8.314 J/mol K
- T reaction temperature, K

The linear relationship of Equation (4.18), for each of the four reactions, is shown in Figures 4.5 to 4.8. A summary of the Arrhenius parameters is given in Table 4.6. The activation energy for the reaction of naphtha to gas was 215 kJ/mol, which is close to 220.8 kJ/mol obtained by Kumar and Kunzru (1985) and within the range of 212 to 228 kJ/mol found by van Damme and Froment (1981).

## 4.5 Overall Reaction Rate

Although the activation energy for the naphtha lump reacting to form gas compares favourably with the literature, there is no data in the literature with which the results of the four-lump reaction scheme can be directly compared. Therefore, calculations have been performed based on a simplified overall reaction for which comparison to the literature is possible. This first order overall reaction is assumed to be:

$$k_{o}$$
 Gas Oil  $\longrightarrow$  Products (Naphtha, Gas and Coke)

The initial weight percent of LGO was 94 and naphtha was six percent. Repeating similar calculations and regressions on the Microsoft EXCEL 2000 solver function, an







Figure 4.6 Activation Energy Evaluation (Naphtha > Gas)



Figure 4.7 Activation Energy Evaluation (LGO→Gas)





LGO → Naphtha	E <sub>1</sub> , kJ/mol	173
	$A_1, s^{-1}$	3.22×10 <sup>10</sup>
Naphtha>Gas	E <sub>2</sub> , kJ/mol	215
	A <sub>2</sub> , s <sup>-1</sup>	2.41×10 <sup>13</sup>
LGO → Gas	E <sub>3</sub> , kJ/mol	83
	A <sub>3</sub> , s <sup>-1</sup>	1.23×10 <sup>4</sup>
LGO $\longrightarrow$ Coke	E4, kJ/mol	262
	A4, s <sup>-1</sup>	8.81×10 <sup>13</sup>

Table 4.6 Activation Energies and Frequency Factors

overall reaction rate constant can be obtained and results are given in Table 4.7. Based on these results, the overall reaction frequency factor and activation energy were determined to be  $1.9 \times 10^9$  s<sup>-1</sup> and 153 kJ/mol, respectively (see Figure 4.9).

Runs	3	5	2	8	1	4	6	7
Temperature, °C	500	500	530	530	550	550	550	550
1000×k <sub>o</sub> , s <sup>-1</sup>	103	89	233	260	373	393	420	437

Table 4.7 Overall Thermal Cracking Reaction Rate Constant

The molecular weight of the gas oil fraction (>196°C) in the feed gas oil is approximately 221, which is very close to n-hexadecane (MW = 226). Fairburn *et al.* (1990) used a Curie point pyrolyser to study ultrapyrolysis of n-hexadecane. She found that the activation energy of n-hexadecane pyrolysis was 164 kJ/mol. The overall activation energy of this study (at 153 kJ/mol) is quite close to this value.

It should be noted that LGO thermal cracking is a very complex process and it is almost impossible to identify all the chemical species present in the feedstock and study their chemical reactions. The lumping scheme represents an important tool to simplify the model. These simplifications lead to some errors in the model predictions. However, as results of overall reaction kinetic parameters are very close to those of previous



Figure 4.9 Overall Activation Energy Evaluation

researchers using similar model feed, it can therefore be inferred that the proposed fourlump model is reasonable and can be used to predict the product distribution.

# 4.6 **Product Distribution Prediction**

Using calculated activation energies and frequency factors of four hypothetical reactions, shown in Figure 4.4, a reaction rate constant at any temperature within the range tested experimentally can be obtained.

Figures 4.10 to 4.12 are the results of model predictions at several typical operating temperatures. According to the proposed model, the desired product, naphtha, is an intermediate product from gas oil to gas. Therefore, there should exist optimal conditions for which maximum production of naphtha is possible. A summary of the optimal reaction time at different temperatures is shown in Table 4.8.

Temperature, °C	500	530	550
Residence time, s	10	3.6	1.8
Maximum Naphtha Yield, wt% of product	29	28	26

 Table 4.8 Optimal Reaction Times at Different Temperatures



Figure 4.10 Component Mass Percent vs. Residence Time at 500°C



Figure 4.11 Component Mass Percent vs. Residence Time at 530°C


Figure 4.12 Component Mass Percent vs. Residence Time at 550°C

From Figures 4.10 to 4.12, it is also found that coke formation is very low. This is expected because the feed has been hydrotreated. Gas is the other ultimate by-product aside from coke. Gas production increases continuously with residence time.

### **CHAPTER 5**

### **Conclusions and Recommendation**

### 5.1 Conclusions

A helical coil reaction system was capable of studying the reaction kinetics of the hydrotreated light gas oil thermal cracking. The hydrotreated light gas oil thermal cracking reaction was studied at three different temperature levels, 500°C, 530°C and 550°C. A kinetic analysis has been performed by assuming a first order overall decomposition model for the light gas oil thermal cracking reaction. The activation energy of this reaction was evaluated to be 153 kJ/mol. The result is very close to the 164 kJ/mol obtained by Fairburn et al. (1990) for n-hexadecane pyrolysis in a Curie point pyrolyser. A four-lump kinetic model was developed and evaluated to give a better understanding of the product distribution. According to the experimental data, the activation energy for the reaction of gas oil to naphtha was 173 kJ/mol, for the reaction of naphtha to gas was 215 kJ/mol, for the reaction of gas oil to gas was 83 kJ/mol and for the reaction of gas oil to coke was 262 kJ/mol. The activation energy for the reaction of naphtha to gas is close to 220.8 kJ/mol obtained by Kumar and Kunzru (1985) and within the range of 212 to 228 kJ/mol found by van Damme and Froment (1981). Product distributions for different reaction temperatures were predicted using the proposed kinetic model. It was found that at 500°C, the optimal residence time was 10 seconds with a maximum naphtha production of 29 wt%; at 530°C, the optimal residence time was 3.6 seconds with a maximum naphtha production of 28 wt% and at 550°C, the optimal residence time was 1.8 seconds with a maximum naphtha production of 26 wt%.

# 5.2 Recommendation

Although boiling point range is of primary concern to industry, a model based on reactivity of different hydrocarbon structures may result in a more predictive model. With a more detailed analysis of feed and products, it may be possible to understand the roles that different types of carbon play in thermal cracking reactions. Among them, PONA (paraffins, olefins, naphthenes, aromatics) analysis on a GC and NMR spectroscopy may be the most useful tools.

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### Appendix A

### **Mass Balance Calculation for Different Runs**

Table A.1 is the SimDist analysis of the whole feed light gas oil. An estimation of its average MW is given based on the MW of normal paraffins. The weight percents of naphtha fraction (<196°C) and gas oil fraction (>196°C) are also shown. Table A.2 is the average MW of LGO pseudo-component (>196°C) in the feed and a comparison to n-hexadecane. Tables A.3 to A.10 are mass balance calculations for the Runs #1 to #8, including SimDist results of reaction liquid products and GC analysis results for the reaction gas bags. The sum of Yi for the gas analysis includes only the hydrocarbons; the balance is nitrogen. Compositions of pseudo-components are calculated using Equations (4.5) to (4.8). The residence time was calculated based on Equations (4.1) and (4.2).

A Erlenmeyer flask containing 0.5 M Zn(Ac)<sub>2</sub> solution was installed immediately before the WTM (see Figure 3.4) to absorb any H<sub>2</sub>S which could potentially be produced. A KOH solution had been used for Runs #1 and #2. A switch was made to the Zn(Ac)<sub>2</sub> solution, because CO<sub>2</sub> could be absorbed by KOH solution. Runs #1 showed similar CO<sub>2</sub> production to replicate runs. There was only 2 cm contacting length (the KOH solution was shallow), the KOH concentration in the solution was very low (about 0.03 M) and the gas flow rate was high so that not much CO<sub>2</sub> was absorbed. Zn(Ac)<sub>2</sub> solution absorbs  $H_2S$  but not  $CO_2$ . For hydrocarbon feed such as the one used in this study, this absorption step was probably not necessary.

# Table A.1 Molecular Weight Calculation of Whole Feed

E	-	
T.	CC	u

С	#	MW	wt %	mol	mol %	ave MW		
	4	58	0	0	0	0		
	5	72	0.01	0.0001389	0.0002938	0.0211567	MW	212
	6	86	0.03	0.0003488	0.000738	0.06347	X10, wt%	<196°C 6
	7	100	0.04	0.0004	0.0008463	0.0846267	X20, wt%	>196°C 94
	8	114	0.66	0.0057895	0.0122486	1.3963407	X30, wt%	Gas O
	9	128	1.96	0.0153125	0.0323962	4.1467087	X40, wt%	Coke 0
	10	142	3.58	0.0252113	0.0533387	7.5740904	SUM	100
	11	156	5.76	0.0369231	0.078117	12.186246		
	12	170	8.32	0.0489412	0.1035433	17.602355		
	13	184	8.87	0.0482065	0.101989	18.765973		
	14	198	10.35	0.0522727	0.1105917	21.897161		
	15	212	9.57	0.0451415	0.0955044	20.24694		
	16	226	9.71	0.0429646	0.0908988	20,543133		
	17	240	8.81	0.0367083	0.0776626	18.639032		
	18	254	13.02	0.0512598	0.1084488	27.545993		
	20	282	8.64	0.0306383	0.0648205	18.279369		
	22	310	4.82	0.0155484	0.0328952	10.197518		
	24	338	2.66	0.0078698	0.0166499	5.6276761		
	26	366	1.63	0.0044536	0.0094222	3.4485384		
	28	394	0.87	0.0022081	0.0046717	1.8406309		
	30	422	0.47	0.0011137	0.0023563	0.9943638		
	32	450	0.26	0.0005778	0.0012224	0.5500736		
	34	478	0.14	0.0002929	0.0006197	0.2961935		
	36	506	0.09	0.0001779	0.0003763	0.1904101		
	38	534	0.05	9.363E-05	0.0001981	0.1057834		
	40	562	0.04	7.117E-05	0.0001506	0.0846267		
	42	590	0	0	0	0		
SUM			100.36	0.472664	1	212.32841		

SUM

# Table A.2 Molecular Weight Calculation of Feed (>196°C)

# Feed (>196°C)

С#		MW	wt %	normalized	mol	mol%	ave MW
	11	156	5.76	0.06122449	0.0003925	0.0867833	13.538191
	12	170	8.32	0.088435374	0.0005202	0.1150304	19.555165
	13	184	8.87	0.094281463	0.0005124	0.1133037	20.847874
	14	198	10.35	0.110012755	0.0005556	0.1228608	24.326437
	15	212	9.57	0.101721939	0.0004798	0.1060997	22.49314
	16	226	9.71	0.103210034	0.0004567	0.1009832	22.822193
	17	240	8.81	0.093643707	0.0003902	0.0862785	20.706851
1	8	254	13.02	0.138392857	0.0005449	0.1204801	30.601952
	20	282	8.64	0.091836735	0.0003257	0.0720117	20.307286
2	22	310	4.82	0.051232993	0.0001653	0.0365446	11.328833
2	24	338	2.66	0.02827381	8.365E-05	0.0184971	6.2520117
2	26	366	1.63	0.01732568	4.734E-05	0.0104675	3.83112
2	28	394	0.87	0.009247449	2.347E-05	0.0051899	2.0448309
3	0	422	0.47	0.004995748	1.184E-05	0.0026177	1.1046788
3	2	450	0.26	0.002763605	6.141E-06	0.001358	0.6110989
3	4	478	0.14	0.001488095	3.113E-06	0.0006884	0.3290532
3	6	506	0.09	0.000956633	1.891E-06	0.0004181	0.2115342
3	8	534	0.05	0.000531463	9.952E-07	0.0002201	0.117519
4	0	562	0.04	0.00042517	7.565E-07	0.0001673	0.0940152
4	2	590	0	0	0	0	0
SUM			94.08	1	0.0045224	1	221.12378

MW(C16) 226

C #	MW	wt %	mol	mol %	ave MW	•		MW	Yi	MiYi	
4	58	0	0	0	0		CI	16	6.52	104.32	
5	72	0.02	0.0002778	0.0004873	0.0350847		C2=	28	4.48	125.44	
6	86	0.69	0.0080233	0.0140747	1.2104216		C2	30	2.62	78.6	
7	100	3.45	0.0345	0.0605211	6.0521082		C3=	42	4.1	172.2	
8	114	5.03	0.0441228	0.0774017	8.8237984		C4=	56	2.16	120.96	
9	128	5.46	0.0426563	0.0748291	9.5781191		C4	58	0.02	1.16	
10	142	7.02	0.0494366	0.0867234	12.314725		C4H6	54	1.22	65.88	
11	156	9.68	0.0620513	0.1088525	16.980988		C5	72	0.38	27.36	
12	170	11.84	0.0696471	0.1221773	20.770134		Cyc-C5	70	0.06	4.2	
13	184	10.94	0.0594565	0.1043007	19.191323		C6	86	0.05	4.3	
14	198	10.51	0.0530808	0.0931162	18.437002		SUM		21.61	704.42	
15	212	8.78	0.0414151	0.0726518	15.402177		Ave MW (C	as) =	32.596946		
16	226	7.5	0.0331858	0.0582157	13.156757						
17	240	5.68	0.0236667	0.0415169	9.9640507						
18	254	7.02	0.0276378	0.0484832	12.314725						
20	282	3.61	0.0128014	0.0224567	6.3327857		outlet fluid				
22	310	1.71	0.0055161	0.0096766	2.9997406		G %	L %	MW(G)	MW(L)	Ave MW
24	338	0.87	0.002574	0.0045153	1.5261838		25.423729	74.576271	32.596946	175.09012	139
26	366	0	0	0	0						
28	394	0	0	0	0		Material Ba	lance			
30	422	0	0	0	0		feed, g	165	SimDist for	Liquid produ	ict
32	450	0	0	0	0		L, g	118.8	<196°C, %	0.22	
34	478	0	0	0	0		G, g	40.5	>196°C, %	0.78	
36	506	0	0	0	0		C, g	0.35	trapped by ra	iyon, g	12.1
38	534	0	0	0	0		recovery	0.968	>C4 in gas b	ag, g	2
40	562	0	0	0	0			g		wt%	
42	590	0	0	0	0		<196°C	37.574	X1	0.2353523	• • • • • • • • • • • • • • • • • • • •
UM		99.81	0.5700493	1	175.09012		>196°C	83.226	X2	0.5213028	
				<u> </u>			G	38.5	X3	0.2411525	
Т	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res t, s	lc	0.35	X4	0.0021923	
550	6	94	0.0003471	0.0002193	212	1.5829728	SUM	159.65		1	

Table A.3 Mass Balance Calculation for Run #1

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Table A, 7 Mass Dalance Calculation 101 Kull #2	Table A.4	Mass	Balance	Calcu	lation	for	Run	#2
-------------------------------------------------	-----------	------	---------	-------	--------	-----	-----	----

outlet lig						_	outlet gas				-
C #	MW	wt %	mol	mol %	ave MW	_		MW	Yi	MiYi	
4	58	0.03	0.0005172	0.0009387	0.0544427		CI	16	3.99	63.84	-
5	72	0.18	0.0025	0.0045369	0.3266559		C2=	28	3.27	91.56	
6	86	1.08	0.0125581	0.0227899	1.9599355		C2	30	2	60	
7	100	2.46	0.0246	0.044643	4.4642975		C3=	42	2.86	120.12	
8	114	3.39	0.0297368	0.0539651	6.1520198		C4=	56	0	0	
9	128	4.48	0.035	0.0635164	8.1301028		C4	58	0.23	13.34	
10	142	6.25	0.0440141	0.0798748	11.342219		C4H6	54	0	0	
11	156	8.71	0.0558333	0.1013238	15.806517		C5	72	0.17	12.24	
12	170	11.12	0.0654118	0.1187063	20.180077		Cyc-C5	70	0	0	
13	184	10.64	0.0578261	0.1049402	19.308994		C6	86	0.11	9.46	
14	198	10.76	0.0543434	0.09862	19.526765		SUM		12.63	370.56	
15	212	9.03	0.0425943	0.0772983	16.387239		Ave MW (G	ias) =	29.339667		
16	226	8.11	0.035885	0.0651224	14.717664						
17	240	6.55	0.0272917	0.0495277	11.886646						
18	254	8.58	0.0337795	0.0613016	15.570599						
20	282	4.79	0.0169858	0.0308251	8.6926769		outlet fluid				
22	310	2.26	0.0072903	0.0132302	4.1013465		G %	L%	MW(G)	MW(L)	Ave N
24	338	1.12	0.0033136	0.0060134	2.0325257		13.425926	86.574074	29.339667	181.67513	
26	366	0.57	0.0015574	0.0028263	1.0344104						
28	394	0	0	0	0		Material Ba	lance			
30	422	0	0	0	0		feed, g	159.2	SimDist for	Liquid produ	ict
32	450	0	0	0	0		L, g	130.9	<196°C, %	0.18	
34	478	0	0	0	0		G, g	20.3	>196°C, %	0.82	
36	506	0	0	0	0		C, g	0.2	trapped by ra	iyon, g	
38	534	0	0	0	0		recovery	0.951	>C4 in gas b	ag, g	
40	562	0	0	0	0			g		wt%	
42	590	0	0	0	0		<196°C	34.812	X1	0.2299339	
SUM		100.11	0.5510385	1	181.67513		>196°C	97.088	X2	0.6412682	
							G	19.3	X3	0.1274769	
T	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res L s	С	0.2	X4	0.001321	
530	6	94	0.0003471	0.0002118	212	1.6387516	SUM	151.4		1	

	MW	Yi	MiYi
CI	16	3.99	63.84
C2=	28	3.27	91.56
C2	30	2	60
C3=	42	2.86	120.12
C4=	56	0	0
C4	58	0.23	13.34
C4H6	54	0	0
C5	72	0.17	12.24
Cyc-C5	70	0	0
C6	86	0.11	9.46
SUM		12.63	370.56
Ave MW (Gas)	= 1	9.339667	

801
0

utlet lig							outlet gas			
C #	MW	wt %	mol	mol %	ave MW	-		MW	Yi	MiYi
4	58	0.01	0.0001724	0.0003346	0.0194074	-	C1	16	1.69	27.04
5	72	0.07	0.0009722	0.0018868	0,1358515		C2=	28	l.02	28.56
6	86	0.3	0.0034884	0.00677	0.5822206		C2	30	1.6	48
7	100	0.73	0.0073	0.0141674	1.4167369		C3=	42	1.01	42.42
8	114	1.41	0.0123684	0.0240038	2.736437		C4=	56	0.48	26.88
9	128	2.78	0.0217188	0.0421503	5.3952446		C4	58	0.19	11.02
10	142	4.79	0.0337324	0.0654657	9.2961229		C4H6	54	0.33	17.82
11	156	7.56	0.0484615	0.094051	14.67196		C5	72	0.094	6.768
12	170	10.7	0.0629412	0.1221522	20.76587		Cyc-C5	70	0.011	0.77
13	184	11.12	0.0604348	0.1172879	21.580979		C6	86	0.014	1.204
14	198	12.3	0.0621212	0.1205608	23.871046		SUM		6.439	210.482
15	212	10.86	0.0512264	0.0994169	21.076387		Ave MW (C	Gas) =	32.688616	
16	226	10.14	0.0448673	0.0870755	19.679058					······································
17	240	8.41	0.0350417	0.0680066	16.321585					
18	254	10.48	0.0412598	0.0800744	20.338908					
20	282	5.19	0.0184043	0.0357178	10.072417		outlet fluid			
22	310	2.11	0.0068065	0.0132095	4.0949519		G %	L %	MW(G)	MW(L)
24	338	0.92	0.0027219	0.0052825	1.7854766		6.371329	93.628671	32.688616	194.71399
26	366	0.45	0.0012295	0.0023862	0.873331					
28	394	0	0	0	0		Material Ba	lance		
30	422	0	0	0	0		feed, g	209.7	SimDist for	Liquid produ
32	450	0	0	0	0		L, g	188.1	<196°C, %	0.1
34	478	0	0	0	0		G, g	12.8	>196°C, %	0.9
36	506	0	0	0	0		C, g	0.05	trapped by r	ayon, g
38	534	0	0	0	0		recovery	0.958	>C4 in gas b	ag, g
40	562	0	0	0	0			g		wt%
42	590	0	0	0	0		<196°C	30.47	X1	0.1516298
UМ		100.33	0.5152686	1	194.71399		>196°C	158.13	X2	0.7869122
							G	12.3	X3	0.0612093
Т	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res L, s	с	0.05	X4	0.0002488
500	6	94	0.0003471	0.0002006	212	1.7307183	SUM	200.95		1

Table A.5 Mass Balance Calculation for Run #3

<b></b>	
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9	

Ave MW

184

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0.5

outlet liq							outlet gas				
C #	MW	wt %	mol	mol %	ave MW	-		MW	Yi	MiYi	
4	58	0.03	0.0005172	0.000903	0.0523742		CI	16	6.61	105.76	•
5	72	0.21	0.0029167	0.0050919	0.3666195		C2=	28	4.66	130.48	
6	86	1.62	0.0188372	0.0328861	2.8282079		C2	30	2.69	80.7	
7	100	3.66	0.0366	0.0638965	6.3896549		C3=	42	4.41	185.22	
8	114	4.54	0.0398246	0.069526	7.9259654		C4=	56	2.3	128.8	
9	128	5.23	0.0408594	0.0713326	9.1305724		C4	58	0.02	1.16	
10	142	6.66	0.0469014	0.0818808	11.627077		C4H6	54	1.32	71.28	
11	156	8.92	0.0571795	0.0998244	15.572602		C5	72	0.41	29.52	
12	170	11.07	0.0651176	0.1136829	19.326087		Cyc-C5	70	0.07	4.9	
13	184	10.48	0.0569565	0.0994351	18.296061		C6	86	0.05	4.3	
14	198	10.3	0.0520202	0.0908173	17.981816		SUM		22.54	742.12	
15	212	8.7	0.0410377	0.071644	15.188524		Ave MW (C	Gas) =	32.924579		
16	226	7.72	0.0341593	0.0596355	13.477633						
17	240	6.04	0.0251667	0.0439362	10.544676						
18	254	7.62	0.03	0.0523742	13.303052						
20	282	3.93	0.0139362	0.0243299	6.8610229		outlet fluid				_
22	310	1.75	0.0056452	0.0098554	3.0551629		G %	L %	MW(G)	MW(L)	A
24	338	0.88	0.0026036	0.0045453	1.5363105		26.078235	73.921765	32.924579	175.24414	
26	366	0.42	0.0011475	0.0020034	0.7332391						
28	394	0.22	0.0005584	0.0009748	0.3840776		Material Ba	lance			
30	422	0.13	0.0003081	0.0005378	0.226955		feed, g	208.2	SimDist for	Liquid produ	ict
32	450	0.08	0.0001778	0.0003104	0.1396646		L, g	147.4	<196°C, %	0.22	
34	478	0.06	0.0001255	0.0002191	0.1047484		G, g	52	>196°C, %	0.78	
36	506	0.04	7.905E-05	0.000138	0.0698323		С, g	0.4	trapped by ra	ayon, g	
38	534	0.03	5.618E-05	9.808E-05	0.0523742		recovery	0.960	>C4 in gas b	ag, g	
40	562	0.02	3.559E-05	6.213E-05	0.0349161			g		wt%	
42	590	0.02	3.39E-05	5.918E-05	0.0349161		<196°C	49.624	X1	0.2483684	
SUM		100.38	0.5728009	1	175.24414		>196°C	100.776	X2	0.5043844	
<u></u>							G	49	X3	0.2452452	
T	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res t, s	с	0.4	X4	0.002002	
550	6	94	0.0003471	0.0002194	212	1.5821185	SUM	199.8		1	

 Table A.6
 Mass Balance Calculation for Run #4

110

Ave MW

138

18.2 3

C #	MW	wt %	mol	mol %	ave MW			MW	Yi	MiYi	
4	58	0	0	0	0	•	C1	16	1.71	27.36	
5	72	0.04	0.0005556	0.0011011	0.0792818		C2=	28	1.03	28.84	
6	86	0.13	0.0015116	0.0029961	0.257666		C2	30	1.61	48.3	
7	100	0.29	0.0029	0.0057479	0.5747934		C3=	42	1.02	42.84	
8	114	0.96	0.0084211	0.0166909	1.9027644		C4=	56	0.83	46.48	
9	128	2.56	0.02	0.0396409	5.0740383		C4	58	0.19	11.02	
10	142	4.78	0.033662	0.0667196	9.4741808		C4H6	54	0	0	
11	156	7.65	0.0490385	0.0971965	15.162653		C5	72	0.095	6.84	
12	170	10.77	0.0633529	0.1255685	21.346638		Cyc-C5	70	0.012	0.84	
13	184	11	0.0597826	0.1184919	21.802508		C6	86	0	0	
14	198	11.98	0.0605051	0.1199238	23.744913		SUM		6.497	212.52	
15	212	10.39	0.0490094	0.097139	20.59346		Ave MW (C	Gas) =	32.710482		
16	226	9.67	0.0427876	0.084807	19.166387		<u></u>				
17	240	8.1	0.03375	0.0668941	16.054574						
18	254	10.61	0.0417717	0.0827933	21.02951						
20	282	5.99	0.0212411	0.0421009	11.872457		outlet fluid				
22	310	2.86	0.0092258	0.018286	5.6686521		G %	L %	MW(G)	MW(L)	Ave MW
24	338	1.37	0.0040533	0.0080337	2.7154033		5.8958214	94.104179	32.710482	198.71995	189
26	366	0.74	0.0020219	0.0040074	1.4667142						
28	394	0.37	0.0009391	0.0018613	0.7333571		Material Ba	lance	····		
30	422	0	0	0	0		feed, g	182	SimDist for I	Liquid produ	ct
32	450	0	0	0	0		L, g	164.4	<196°C, %	0.09	
34	478	0	0	0	0		G, g	10.3	>196°C, %	0.91	
36	506	0	0	0	0		С, в	0.05	trapped by ra	iyon, g	9.6
38	534	0	0	0	0		recovery	0.960	>C4 in gas b	ag, g	0.4
40	562	0	0	0	0			g		wt%	
42	590	0	0	0	0		<196°C	23.932	X1	0.1369499	
JM		100.26	0.5045291	1	198.71995		>196°C	140.868	X2	0.8061116	
							G	9.9	X3	0.0566524	
Т	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res t, s	c	0.05	X4	0.0002861	
500	6	94	0.0003471	0.0002007	212	1.7292161	SUM	174.75		1	

Table A.7	Mass E	Balance	Calculation	1 for Run	#5
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outlet lig							outlet gas				
C #	MW	wt %	mol	mol %	ave MW	_		MW	Yi	MiYi	-
4	58	0.06	0.0010345	0.0017315	0.1004254	ļ	C1	16	5 5.87	93.92	•
5	72	0.27	0.00375	0.0062766	0.4519143		C2=	28	3.82	106.96	
6	86	2.15	0.025	0.0418439	3.5985766	<b>,</b>	C2	30	) 1.61	48.3	
7	100	4.54	0.0454	0.0759885	7.5988548	;	C3=	42	3.58	150.36	
8	114	5.28	0.0463158	0.0775214	8.8374347	1	വ	44	0.42	18.48	
9	128	5.96	0.0465625	0.0779343	9.9755892		C4=	56	i 0	0	
10	142	7.46	0.0525352	0.0879312	12.486224		C4	58	0.23	13.34	
11	156	9.8	0.0628205	0.1051462	16.402814		C4H6	54	0	0	
12	170	11.85	0.0697059	0.1166707	19.834015		C5	72	2 0.72	51.84	
13	184	10.87	0.0590761	0.098879	18.193734		C6	86	i 0	0	
14	198	10.14	0.0512121	0.0857166	16.971892		SUM		16.25	483.2	
15	212	8.25	0.0389151	0.0651344	13.808492		Ave MW (C	Gas) =	29.735385		•
16	226	7.03	0.0311062	0.0520642	11.766509						•
17	240	5.21	0.0217083	0.0363345	8.7202717						
18	254	6.27	0.024685	0.0413167	10.494454						
20	282	3.1	0.0109929	0.0183995	5.1886454		outlet fluid				
22	310	1.37	0.0044194	0.0073969	2.2930465		G %	L%	MW(G)	MW(L)	Ave MW
24	338	0.75	0.0022189	0.003714	1.2553174		27.777778	72.222222	29.735385	167.97821	13
26	366	0	0	0	0						
28	394	0	0	0	0		Material Ba	lance			
30	422	0	0	0	0		feed, g	109.9	SimDist for	Liquid produ	uct
32	450	0	0	0	0		L, g	75.4	<196°C, %	0.25	
34	478	0	0	0	0		G, g	29	>196°C, %	0.75	
36	506	0	0	0	0		С, g	0.3	trapped by ra	ayon, g	7.
38	534	0	0	0	0		recovery	0.953	>C4 in gas b	ag, g	
40	562	0	0	0	0			g		wt%	
42	590	0	0	0	0		<196°C	27.325	XI	0.2609838	
SUM		100.36	0.5974584	1	167.97821		>196°C	51.075	X2	0.4878223	
							G	26	X3	0.2483286	
Т	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res t, s	С	0.3	X4	0.0028653	
550	6	94	0.0003471	0.0002219	212	1.5645645	SUM	104.7		1	

 Table A.8
 Mass Balance Calculation for Run #6

Tuble 11.7 Muss Bulance Curculation for Run #7	Table A.9	Mass Ba	lance Calcu	lation fo	r Run #7
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outlet lig						_	outlet gas				
C #	MW	wt %	mol	mol %	ave MW	_		MW	Yi	MiYi	-
4	58	0.05	0.0008621	0.0014599	0.0846755	-	Cl	16	7.29	116.64	
5	72	0.24	0.0033333	0.005645	0.4064424		C2=	28	4.78	133.84	
6	86	1.89	0.0219767	0.0372178	3.200734		C2	30	2.1	63	
7	100	4.3	0.043	0.0728209	7.2820933		C3=	42	4.3	180.6	
8	114	5.16	0.0452632	0.0766536	8.7385119		C3	44	0.44	19.36	
9	128	5.81	0.0453906	0.0768695	9.8392934		C4=	56	0	0	
10	142	7.24	0.0509859	0.0863452	12.261013		C4	58	0.32	18.56	
11	156	9.53	0.0610897	0.1034561	16.139151		C4H6	54	0	0	
12	170	11.58	0.0681176	0.1153579	19.610846		C5	72	0.96	69.12	
13	184	10.74	0.0583696	0.0988494	18.188298		C6	86	0	0	
14	198	10.16	0.0513131	0.0868993	17.206062		SUM		20.19	601.12	
15	212	8.44	0.0398113	0.0674209	14.293225		Ave MW (C	Gas) =	29.773155		
16	226	7.37	0.0326106	0.0552264	12.481169						
17	240	5.58	0.02325	0.0393741	9.4497861						
18	254	6.78	0.0266929	0.0452047	11.481998						
20	282	3.28	0.0116312	0.0196976	5.554713		outlet fluid				
22	310	1.39	0.0044839	0.0075935	2.353979		G %	L %	MW(G)	MW(L)	Ave MW
24	338	0.78	0.0023077	0.0039081	1.3209378		24.927536	75.072464	29.773155	169.89293	135
26	366	0	0	0	0						
28	394	0	0	0	0		Material Ba	lance			
30	422	0	0	0	0		feed, g	143.2	SimDist for	Liquid produ	ict
32	450	0	0	0	0		L, g	103.6	<196°C, %	0.25	
34	478	0	0	0	0		G, g	34.4	>196°C, %	0.75	
36	506	0	0	0	0		C, g	0.3	trapped by ra	iyon, g	10
38	534	0	0	0	0		recovery	0.966	>C4 in gas b	ag, g	3.9
40	562	0	0	0	0			g		wt%	
42	590	0	0	0	0		<196°C	37.3	XI	0.2697035	
SUM		100.32	0.5904896	1	169.89293		>196°C	70.2	X2	0.5075922	
							G	30.5	X3	0.2205351	
Т	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res t, s	С	0.3	X4	0.0021692	
550	6	94	0.0003471	0.0002454	212	1.4145608	SUM	138.3		1	

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pil *	A CONTRACTOR	× 14		mot %	ave MW		outlet gas	MM	Х	MIYI	
	58	0.02	0.0003448	0.0006207	0.0360027		G	16	3.57	57.12	
5	12	0.1	0.0013889	0.0025002	0.1800136		g Ω	28	2.48	69.44	
9	<b>8</b> 8	0.86	0.01	0.0180014	1.5481171		8	30	0.96	28.8	
2	100	2.62	0.0262	0.0471636	4.7163569		Ë	42	1.99	83.58	
~	114	3.9	0.0342105	0.0615836	7.0205312		ខ	4	0.22	9.68	
6	128	5.02	0.0392188	0.0705991	9.0366838		<u>₽</u>	56	0	0	
0	142	6.68	0.0470423	0.0846825	12.02491		2	58	1.1	63.8	
_	156	9.02	0.0578205	0.1040848	16.237229		C4H6	54	0	0	
7	170	11.24	0.0661176	0.1190208	20.233531		ა	22	0.5	36	
ŝ	184	10.63	0.0577717	0.103997	19.135448		ප	86	0	0	
4	198	10.38	0.0524242	0.0943708	18.685414		SUM		10.82	348.42	
S	212	8.7	0.0410377	0.0738735	15.661185		Ave MW (G	(as) =	32.201479		
9	226	7.84	0.0346903	0.0624472	14.113068						
7	240	6.25	0.0260417	0.0468785	11.250851						
~	254	8.22	0.0323622	0.0582564	14.79712						
0	282	4.61	0.0163475	0.0294278	8.2986279		outlet <b>Auid</b>				
5	310	2.23	0.0071935	0.0129494	4.0143037		0% 0	r%	MW(G)	MW(L)	Ave MW
4	338	1.21	0.0035799	0.0064443	2.1781648		12.767857	87.232143	32.201479	180.30164	161
9	366	0.63	0.0017213	0.0030986	1.1340858						
80	394	0	0	0	0		Material Ba	lance			
0	422	0	0	0	0		feed, g	119.8	SimDist for I	Liquid produc	Ħ
2	450	0	0	0	0		L, g	97.7	<196°C, %	0.19	
4	478	0	0	0	0		G, g	14.3	>196°C, %	0.81	
9	506	0	0	0	0		ე ც	0.1	trapped by ra	tyon, g	6.1
~	534	0	0	0	0		recovery	0.936	>C4 in gas bu	ag. g	1.5
0	562	0	0	0	0			ల		W1%	
2	590	0	0	0	0		<196°C	25.004	XI	0.2230508	
		100.16	0.5555135	-	180.30164		>196°C	74.196	X	0.6618733	
							U	12.8	£X	0.1141838	
	X10	X20	V(Reactor)	v, m^3/s	MW(feed)	Res t, s	c	0.1	X4	0.0008921	
	9	Ł	0.0003471	0.0002576	212	1.347688	SUM	112.1		-	

### Appendix B

### **Temperature Profile for Different Runs**

Figures B.1 to B.8 show the temperature profile along with time during the Runs #1 to #8 respectively. The temperature data were obtained by the LabView on-line data acquisition system once every two seconds from thermocouples #19 (inlet) and #20 (outlet). The average of the reactor inlet and outlet temperature (dashed lines) in the figures was used as reaction temperature.

Figure B.1 shows the different stages during an experiment and how the reaction temperature was evaluated.

Figure B.1 shows the temperature of the inlet and outlet fluid. Nitrogen had been purging before feed oil started. After feed oil entered the reactor, it affected the reactor fluid flow rate and caused the dynamic stage. The reaction temperature was determined using the steady state interval shown in the figure B.1. Nitrogen continued to purge after the feed oil was stopped.















Figure B.4 Temperature Profile for Run #4



Figure B.5 Temperature Profile for Run #5



Figure B.6 Temperature Profile for Run #6



Figure B.7 Temperature Profile for Run #7





### Appendix C

# Pump #2 and Pump #3 Calibration

Figure C.1 shows the calibration results for the pumps #2 and #3. The pump had a knob with scale ranging from 0 to 100. These two pumps were set in parallel and the calibration was done with both pumps on and at the same setting on the scale. The pumps were stabilized with hydraulic oil circulating in a recycle loop for one half hour and then the flow was opened to the transfer cylinder for 10 minutes before the calibration for each point.





### Appendix D

### Valve Switching Scheme for Gas Analysis on GC

Two valves (#1 and #2) were installed in a heated valve box on top of the HP 6980 GC oven. Valve #1 has ten ports and valve #2 has six ports. These pneumatic valves were automatically actuated.

Normally the valves were in the OFF position, with the shaft rotated counter-clockwise. Figure D.1 shows column connection sequence with both valves in OFF position. When the valve is switched clockwise, it is the ON mode. For example, for valve #1 in Figure D.1, when it is in OFF mode, port 2 and 3, 4 and 5, 6 and 7, 8 and 9, 10 and 1 are connected. Once valve #1 is turned on, port 1 and 2, 3 and 4, 5 and 6, 7 and 8, 9 and 10 are connected. Therefore, the columns' relative position in the sequence changes. This strategy was used to realize an effective separation of CO and CO<sub>2</sub>. Table D.1 illustrates the operating valve switching sequence, corresponding hydrocarbon position and emerging sequence in the columns at different times. Figure D.2 shows the valve timing logic. The MS column and its contents are shown on the left, while the PLOT Q column and its contents are shown on the right of Figure D.2.




Valve 2 (OFF)

Valve 1 (OFF)

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Time	Valve #1	Valve #2	Flow/Sample Status
Initial	OFF	OFF	Helium flow through MS to Plot Q.
Injection	OFF	OFF	Sample trapped in 25 µl sample loop.
0.0 min	ON	OFF	Light gases to CO through Plot Q to MS.
1.35 min	ON	ON	Plot Q isolated, containing $CO_2$ and heavier hydrocarbons. Light gases to CO are analyzed by TCD.
4.0 min	OFF	ON	Flow reversed on MS, $CO_2$ and heavier hydrocarbons still trapped on Plot Q.
4.1 min	OFF	OFF	Flow through MS then Plot Q, $CO_2$ and heavier hydrocarbons go to TCD.

Table D.1 Valve Status and Flow/Sample Status



Figure D.2 Valve Timing Logic

### Appendix E

## Estimation of the Reynolds Number and Heat Transfer Coefficient

Equation E.1 and E.2 were used to estimate the Reynolds number.

$$\operatorname{Re} = \frac{du\rho}{\mu} = \frac{dG}{\mu} \tag{E.1}$$

$$G = \frac{\dot{m}}{A} = \frac{4\dot{m}}{\pi d^2} \tag{E.2}$$

where:

Re	Reynolds number
d	reactor tube ID, m
u	fluid velocity, m/s
ρ	fluid density, kg/m <sup>3</sup>
μ	fluid viscosity, Pa·s
G	fluid mass flux, kg/m <sup>2</sup> ·s
'n	fluid mass flow rate, kg/s
A	cross-section area of the reactor tube, $m^2$

For Run #1, the LGO mass flow rate was 0.1314 g/s and the LGO/N<sub>2</sub> mass ratio was 2.0 (see Appendix G for detailed calculations). To give an estimate of the Reynolds number at the inlet end, the smaller reactor tube ID of 3.34 mm was used to obtain a reactor fluid

mass flux of 22.5 kg/m<sup>2</sup>·s. Nitrogen viscosity at 500°C was found to be  $3.6 \times 10^{-5}$  Pa·s (Perry and Green, 1997, p.2-321). The viscosity of the hydrocarbon gases in the reactor was estimated to be  $1.6 \times 10^{-5}$  Pa·s based on molecular weight (200g/mol) and temperature (GPSA data book, 1994, p.23-39). An average reactor fluid viscosity of  $2.6 \times 10^{-5}$  Pa·s was used to calculate the Reynolds number. It was found to be 2900. By considering the enhancement of helical geometry, it can be assumed that the reactor fluid is in the turbulent regime.

The Colburn equation was used to calculate the heat transfer coefficient (Coulson and Richardson, 1990, p. 343).

$$Nu = 0.023 \,\mathrm{Re}^{0.8} \,\mathrm{Pr}^{0.33} \tag{E.3}$$

$$Nu = \frac{hd}{k} \tag{E.4}$$

where:

Nu	Nusselt number
Re	Reynolds number
Pr	Prandtl number
h	heat transfer coefficient, W/m <sup>2</sup> K
k	thermal conductivity, W/mK

When gases are heated or cooled, the Prandtl group usually has a value of about 0.74, substitution of Pr = 0.74 in equation E.3 gives the equation (Coulson and Richardson, 1990, p. 344):

$$Nu = 0.02 \,\mathrm{Re}^{0.8}$$
 (E.5)

The thermal conductivities of nitrogen and hydrocarbon gases at 500°C are 0.056 W/mK and 0.05 W/mK, respectively (GPSA data book, 1994, p.23-47). An average value of 0.053 W/mK was used for the reactor fluid thermal conductivity. From the above equations, the heat transfer coefficient can be calculated as  $187 \text{ W/m}^2\text{K}$  for straight tube. With a helical coil, somewhat improved heat transfer is obtained for the same physical conditions. The following equation was used to account for this effect (Coulson and Richardson, 1990, p. 399) and the heat transfer coefficient for the coil geometry was found to be 210 W/m<sup>2</sup>K.

$$h(coil) = h(straight \ pipe) \left(1 + 3.5 \frac{d(tube \ ID)}{d(helix)}\right)$$
(E.6)

From the energy balance equation:

$$\frac{\Delta T}{L} = \frac{\pi dh (T_{wall} - T_{fluid})}{\dot{m}c_p} \tag{E.7}$$

where:

- c<sub>p</sub> heat capacity of reaction fluid, J/kgK
- $\frac{\Delta T}{L}$  fluid temperature change along the reactor tube, K/m

The heat capacities of nitrogen and hydrocarbon gases at 500°C are 1050 J/kgK and 3100 J/kgK (GPSA data book, 1994, p.23-3), respectively. An average value of 2075 J/kgK was used for the reactor fluid heat capacity. From Equation E.7, the fluid temperature rose at a rate of 810 K/m along the reactor tube. To heat the fluid entering the reactor from 350°C to 500°C would require 0.185 m or approximately 20 cm.

It should be noted that the proceeding calculations are based upon wall to gas heat transfer. Boiling heating transfer rates are generally higher or on the same order of magnitude as wall to gas heat transfer rates. Therefore, the lower bound of wall to gas heat transfer has been used in the analysis.

#### Appendix F

#### Estimation of the Pressure Drop along the Reactor Tube

The pressure drop along the reactor tube can be calculated using the following equation (Coulson and Richardson, 1990, p. 54).

$$\Delta P = 4f \frac{L}{d} \rho \ u^2 = 4f \frac{L}{d} G u \tag{F.1}$$

where:

dreactor tube ID, mffriction factorGfluid mass flux, kg/m²·sLreactor length, mufluid velocity, m/s

For Run #1, the average fluid velocity can be calculated using the residence time obtained in Appendix A and the reactor length of 18 m. Here a residence time of 1.73 s was used. G was calculated to be 22.5 kg/m<sup>2</sup>·s (Equation E.2). The Blasius equation (Coulson and Richardson, 1990 p. 53) was used to calculate the friction factor.

$$f = 0.0396 \,\mathrm{Re}^{-0.25} \tag{F.2}$$

Assuming a Reynolds number of 2900 (Appendix E), the pressure drop along the reactor tube was estimated as 27 kPa.

The actual pressure drop must be based upon the actual fluid velocity, which changes along the length of the reactor. The velocity tends to increase due to cracking but decreases because of increased diameter in the last half of the reactor. These two effects counteract each other. 27 kPa is estimated to be an upper bound on the pressure drop over the reactor. This is low enough to be neglected in the current study.

#### Appendix G

#### Calculations of the LGO to Nitrogen Ratio

The ideal gas equation of state was used to calculate the nitrogen mass flow rate because of the high temperature and the low pressure.

$$\dot{m}_{N_2} = \frac{P v_{N_2} M_{N_2}}{R T_0} \tag{G.1}$$

where:

 $\dot{m}_{N_2}$ mass flow rate of nitrogen, kg/s $v_{N_2}$ volume flow rate of nitrogen at room temperature, m³/sRgas constant, J/mol KT\_0room temperature, 296 K

For Run #1, the nitrogen volume flow rate is 0.058 L/s at 23°C which is equivalent to a mass flow rate of 0.067 g/s can be obtained. If the mass flow rate of the feed oil is 0.1314 g/s, the LGO to nitrogen mass ratio will be 2.0.

Appendix H

List of Failed Experiments

# Table H.1 Summary of Failed Experiments

Run	Date	Reactor Temperature, °C	Feed Time, s	Comments
1	99-05-26	500	40	Run failed due to high feed flow rate and very short feed time. Poor mass balance.
2	99-06-05	500	-	Forgot to refill the transfer cylinder; feed ran out during bleeding.
3	99-06-17	600	-	Thermocouples were out of order after heating up to 600°C.
4	99-06-23	620	62	Run failed due to high temperature and insufficient packing of rayon. Some liquid products went into piping after the demister and gas bag.
5	99-06-25	580	57	Oil went into the piping after the demister. Feed flow rate was too high.
6	99-07-16	550	60	Run failed because no feed entered the reactor.
7	99-07-28	500	877	Run failed due to no bleeding of feed prior to directing it to the reactor. Feed went through reactor very fast because of elevated preheater pressure. The SimDist results showed no thermal cracking occurred.
8	99-08-08	540	-	No products exited the reactor.
9	99-08-19	540	-	Pump problem, no oil enter the reactor.
10	99-11-23	-	-	LabView did not record temperatures properly (large fluctuations).